Development of Sorbent Materials to Remove Mercury From Liquid Hydrocarbons

BY

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DEDICATED TO

MOTHER AND FATHER

WIFE AND SONS

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TABLE OF CONTENTS

LIST OF TABLES

TABLE **PAGE**

LIST OF FIGURES

FIGURE **PAGE**

Dissertation Abstract

NAME: **Abdullah R. Al-Malki**

TITLE: **Development of Sorbent Materials to Remove Mercury From Liquid Hydrocarbons**

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A new technology for mercury removal from liquid hydrocarbon is of prime importance. Mercury has been considered as a priority hazardous material, due to its adverse effects on human health, industries and the environment. Industrially the mercury metal corrosion effect on gas processing plant systems, particularly the aluminum heat exchangers, is well known and has caused failures over the past several decades. The other issue with mercury is that even at low ppb level, this substance is poisonous to precious catalysts used in petrochemical industrial plants to convert gas and other petroleum based products to chemicals. Several technologies have been implemented to reduce mercury content below 1 ppb in hydrocarbon streams such as gas and light naphtha. However, no technology is available yet to remove mercury from the whole gas condensate or from the crude oil. The removal of mercury from liquid hydrocarbon is a very challenging task as this depends on stream composition, the forms of mercury contents and the water content. This work introduces a new novel sorbents where carbon nanotubes, nanofibers, activated carbon, fly ash and their modified forms with certain metals for the removal of mercury from whole gas condensate. Up to 92% of mercury removal was achieved using these new sorbents. These sorbents are potentially scalable to remove mercury from liquid hydrocarbons under the actual field conditions.

ملخص الرسالة

الأسم: **عبد الله رداد المـالكي .**

عنوان الدراسة **تطوير مواد ماصة لإزالة الزئبق من المواد الهيدروكربونيه السائلة**

التخصص: **كيمياء**

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أصبحت الحاجة إلى تكنولوجيا أفضل لإزالة الزئبق من المواد الهيدروكربونية السائلة واضحة جدا. الزئبق من العناصر الخطرة الأولوية التي لها آثار سلبية على صحة الإنسان وعلى البيئة. ومن المعروف صناعيا تأثير الزئبق على تآكل أنظمة معالجة الغاز، وخاصة المبادلات الحرارية المصنوعة من الألومنيوم والتي تسبب في كثير من المشاكل التشغيليه في العقود القليلة الماضية. ووجود الزئبق ولو بتراكيز منخفضة في حدود تصل الى اجزاء من البليون يؤدي الى تلف المواد الحفازة الثمينة التي يتم استخدامها في معامل صناعة البتروكيماويات لتحويل الغاز والمنتجات البترولية الأخرى الى مواد كيميائية. ولذلك، تم تطبيق العديد من التكنولوجيات لإزالة الزئبق من الغاز والنفثا الخفيفة لتقليل محتواه الي أقل من 1 جزء من البليون. ان إزالة الزئبق من النفط والغاز السائل هي مهمة صعبة للغاية لأن هذا يتوقف على عدة عوامل منها مكونات المادة البترولية، ومصادرها ، ومحتوى الزئبق واشكاله ومحتوى الماء الخ . هذا الدراسه ركزت علي استخدام مواد مختلفة تعتمد علي أنابيب الكربون النانوية وألياف النانو، الكربون المنشط والرماد المتطاير وأشكالها المعدلة مع بعض المعادن. وقد اعطت نتائج اجابيه لامكانيه استخدام هذه المواد لإزالة الزئبق من المواد الهيدروكربونيه السائله ما يصل إلى 92٪. هذه االمواد الماصه يمكن تطبيقها على مستوى اكبر لالزالة الزئبق من المواد الهيدروكربونيه في ظل الظروف الميدانية الفعلية .

CHAPTER 1

INTRODUCTION

Mercury has been recognized as one of the most emitted contaminants in the environment, whether in the atmosphere, water or land. The global atmospheric emission of mercury from all anthropogenic sources in 2005 was estimated to be 1,930 tones [1]. It has been considered a priority hazardous matter due to the adverse effects on human health and the environment. Mercury generally exists in three oxidation states, metallic (Hg^{o}) mercurous (Hg^{+}), and mercuric (Hg^{++}), where the metallic form is the most common, occurring in the atmosphere as elemental vapor, and the mercury organic salts exist in water and sediment [2]. Although mercury is considered very toxic in any form, the mercury methylated form is the most toxic as it can be absorbed by the digestive system. Methylmercury is formed by transforming the inorganic mercury to organic mercury by certain bacteria and accumulated and moved efficiently from one organism to another [2]. Industrially, mercury metal has been known for a long time to have a corrosive effect on gas processing plant systems, particularly heat exchangers made of aluminum, leading to a number of failures in the last several

decades [3]. Therefore, several technologies have been implemented to remove mercury from natural gas to protect the integrity of gas plant systems. The other issue presented by mercury, even at low ppb levels, is that it can poison the precious catalysts that are used in petrochemical industry plants to convert gas and other petroleum based products to chemicals. Therefore, mercury content is now monitored and regulated in crude light-ends, particularly the streams that are used for petrochemical manufacture to protect the catalysts [4]. Some technologies have been implemented to remove mercury from gas and light naphtha to reduce the mercury content below 1 ppb. There is no developed technology to remove mercury from whole gas condensate or crude oil [4].

LITERATURE REVIEW

Mercury is a naturally occurring element that is found in air, water and soil. It exists in several forms: metallic mercury, inorganic mercury compounds, and organic mercury compounds. Mercury is normally released to the environment by two ways; by natural sources such as volcanoes, forest fires, ore, or by human activities (anthropogenic) [5-7]. The anthropogenic mercury source can be classified into primary and secondary sources [6]. Primary anthropogenic are the sources where mercury is produced and transferred to the environment from its geological origin during other activities [5,6]. The two main activities that contribute to this source are mercury mining and other minerals and extraction or burning of fossil fuels that contain mercury as a trace contaminant. Secondary anthropogenic sources are those where emissions occur from the intentional use of mercury in industrial processes, in products, in dental applications, or in artisanal and small-scale gold mining operations [5-7].

Natural sources are responsible for approximately half of atmospheric mercury emissions. The other half is generated by human activities that can be divided into the following estimated percentages: 65% from stationary combustion, of which coal-fired power plants are the largest contributor source [5,6,]. This includes power plants fueled with gas where the mercury has not been removed. Emissions from coal combustion are between one and two orders of magnitude higher than emissions from oil combustion, depending on the country.

Gold is responsible for about 11%; 6.8% from non-ferrous metal production; 6.4% from cement production; 3.0% from waste disposal, including municipal and hazardous waste, and incineration; 3.0% from caustic soda production; 1.4% from pig iron and steel production; 1.1% from mercury production, mainly for batteries; and 2.0% from other sources, Figure 1.1 [6-7].

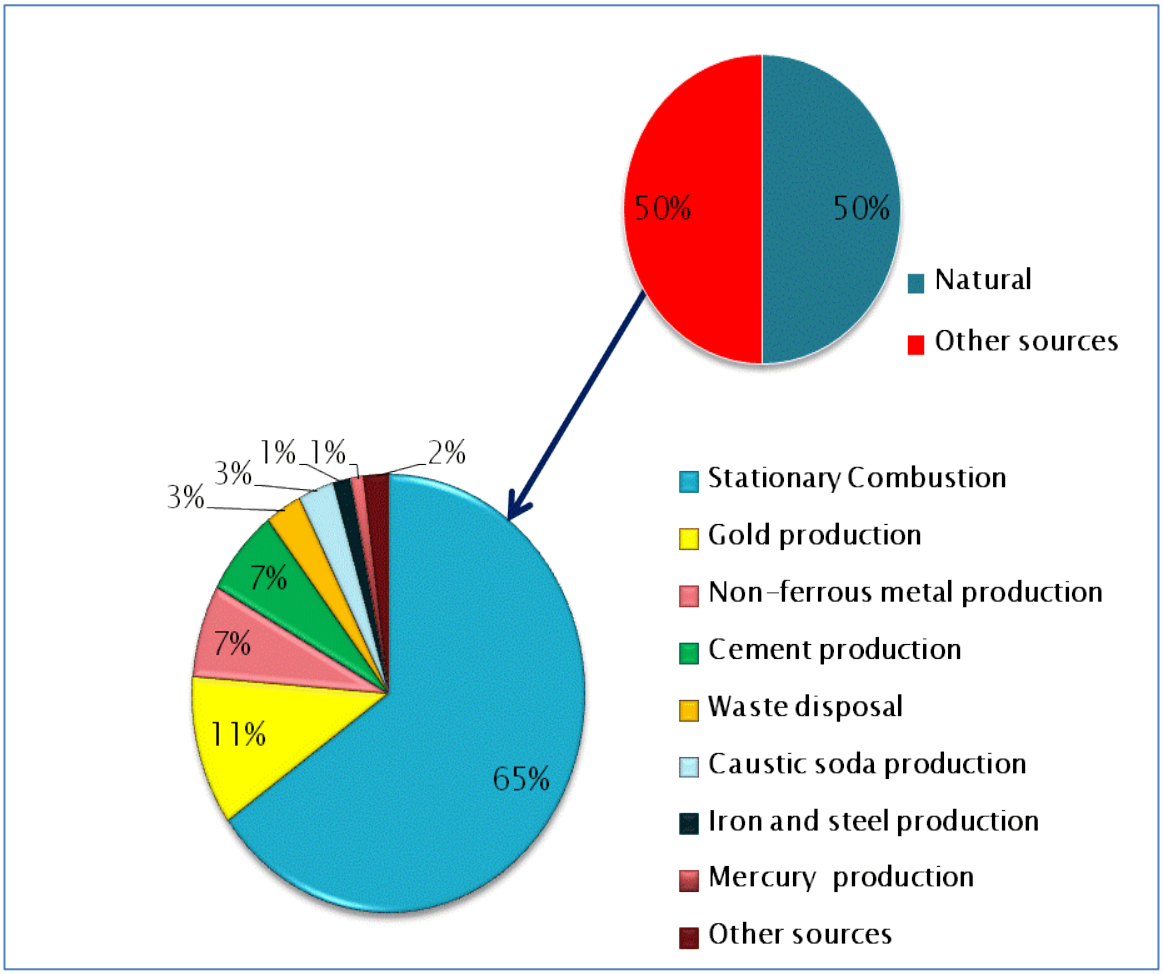


Figure 1.1 Estimated percentage of mercury emission sources

P. Li et al. provided a detailed review of the mercury sources in Asia. The review highlighted that Asia is responsible for over half of global mercury emissions [7]. E.G. Pacyna et al. published recently a very interesting work about the global atmospheric emissions of mercury from human activities [8]. This study indicated that the artisanal and small-scale gold mining remains the largest global use sector for mercury. The trend of mercury usage is projected to continue rising as the gold mining business becomes more attractive. The findings in this study indicated that the mercury is coming from various sources, such as: gold mining, chemical industry, metal smelting, coal combustion, natural resources and agricultural sources.

Mercury generally exits in a trace amount in petroleum and coal. The coal burning is contributing to about 50% of the mercury emission and about 40% resulted from the incineration and about 10% from fuel oil combustion [9]. This source of mercury in the fossil fuels is from the ore in crude oil and gas reservoirs. These reservoirs represent a massive source of all heavy metals contaminants such as Hg, Zn, Cd, As, and Cu, which moved and transferred to the water column and then was produced with crude oil, coal and gas [9,10]. Most of the mercury, about 98%, stayed in the sediments, however, the mercury can be moved to the water during gas or crude oil production in slow process or under the sulfide oxidation and complexation with organic ligands [9,10]. The inorganic form of Hg^{+2} is non-volatile and can go under biotic and abiotic reactions to produce organic compounds such as methylmercury (CH_3Hg^{+}) [10].

Mercury toxicity and its health concerns have been well documented and it is considered to be a global pollutant [11-14]. Mercury as an element, Hg^{o}, has a long residence time in the atmosphere from 0.5-2 years and can be transferred from one place to other remote places, even 1000 km away from its source. Upon releasing Hg metal into the environment is subjected to various chemical reactions and transformations from one form to another, depending on different conditions[12]. Mercury in the form of Hg^{++} is a stable and nonvolatile species that can be converted into methyl mercury, a highly toxic compound. This conversion takes place under oxidation/redaction and methylation-demethylation reactions, involving bacteria process [9]. People are mainly concerned about getting mercury directly from drinking water or indirectly through eating fish that has some mercury as a result of seawater contaminated with mercury [11-13]. Mercury usually exists in three oxidation states, Hg(0), Hg(1+) and Hg (2+). The Hg^{2+} exists in the water or soil environment as salts or organomercury compounds. About 90% of the mercury in the atmosphere exists in elemental mercury [14]. Organic methylmercury is considered to be the most toxic among all other forms as it is believed to damage the immune system, alters genetic and enzyme systems [15,16]. There is no mercury safe level identified for human consumption, however, a maximum mercury concentration of 0.001 ppm is within permissible limits in drinking water [17]. Also the guidelines limit mercury levels in the discharge of industrial wastewater into sewers to be 1 ppb maximum, was implemented starting effective May 1, 2009 [18]. UN committees recommended

new dietary limits for mercury for pregnant women by reducing mercury from 3.3 μg to 1.6 μg per kg body weight per week, to sufficiently protect the developing fetus [19].

The U.S. Environmental Protection Agency promotes policies to eliminate mercury uses, reduce the export of mercury, and significantly reduce mercury exposures at the local, national and international levels. The Agency has issued regulations to reduce mercury releases to air, water and land; and works with a variety of stakeholders, including the waste management and health care industries, to encourage voluntary efforts to reduce or eliminate mercury pollution [20]. The Mercury Export Ban Act of 2008 (MEBA), signed on October 14, 2008, prohibits the export of elemental mercury from the United States, beginning in 2013 [21].

1.1 ISSUES OF MERCURY IN CRUDE, GAS AND GAS CONDENSATE

The presence of trace amount of mercury in oil, natural gas and gas condensate can cause trouble in many parts of the production, transportation, storage and refining systems [22]. The presence of mercury in gas can cause severe corrosion problems where is amalgamate with aluminum leading to complete damage to the heat exchangers. Most of the heat exchangers are made of aluminum that is very susceptible to mercury [23]. The amalgamation with the aluminum causes embrittlement that reduces the mechanical strength leading to unexpected failure and gas leak. Mercury exists in gas, gas condensate and

crude oil can cause serious problems at the downstream operation such as refining and the petrochemical industries [24]. Naphtha produced from gas condensate and crude oil is mostly used as feedstock for the petrochemicals industry. Naphtha is now being monitored for mercury content to protect the petrochemical catalysts [23,24]. This is due to the fact that mercury has the tendency to amalgamate or deposit on catalysts, reducing their efficiency and producing poor quality petrochemical products. The continuous deposition of mercury will ultimately damage the whole catalyst and make its regeneration almost impossible [25]

The mercury in raw petroleum is transferred to the environment by several ways, such as waste water, products, gas and solid waste during the production, transportation and refining process [26]. Although mercury from oil in the refinery is distributed into the different product streams, wastewaters streams typically may contain the major part of the mercury content. When this occurs, wastewaters are not allowed to be discharged in open rivers or oceans because regulatory conformity would not be reached [26,27].

The level of mercury in natural gas can vary significantly depending on the locations and sources as shown in the Table 1.1 [28].

Table 1.1 Average mercury content in natural gas at different regions

Location	**Elemental Hg (mg/m^3)**
South America	0.01-120
East Asia	58-193
North Africa	0.3-130
North Europe	0.01-180
Middle East	1-9
North America	0.001-0.050

Mercury content in crude oil usually ranges from 0.1 to 50 ng/g depending on the crude types and geographical locations. This was demonstrated by a study conducted by Emergencies Science and Technology Division, Canada, from 2003 to 2006, covering 32 types of crude processed in Canadian refineries. The work objective was to monitor the mercury quantity generated from crude oils in a single year. The study concluded that the total amount of mercury in crude oil refined and processed in Canada was estimated to be 227 kg in 2002, 231 kg in 2003, and 240 kg in 2005 [29].

1.2 MERCURY SPECIATION AND DETERMINATION METHODS

Mercury as mentioned early is one of the most toxic elements impacting human and ecosystem. Several forms of the mercury exist in the environment whether in its elemental, inorganic or organic forms with the methylmercury being the most toxic species. The mercury emission from natural or anthropogenic sources is mainly in the elemental form (Hg^{O}), which constitutes more than 99% of the total Hg in the atmosphere. Then mercury in the elemental form is converted by biological or chemical process to other organic and inorganic species. Figure 1.2 demonstrates the biogeochemical cycle of mercury in the environment [30]. The various forms of mercury can be converted from one form to another with most importantly is the conversion to methylmercury (CH_3Hg^{+}), the most toxic form. Ultimately, mercury ends up in the sediments, fish and wildlife, or goes back to the atmosphere by volatilization.

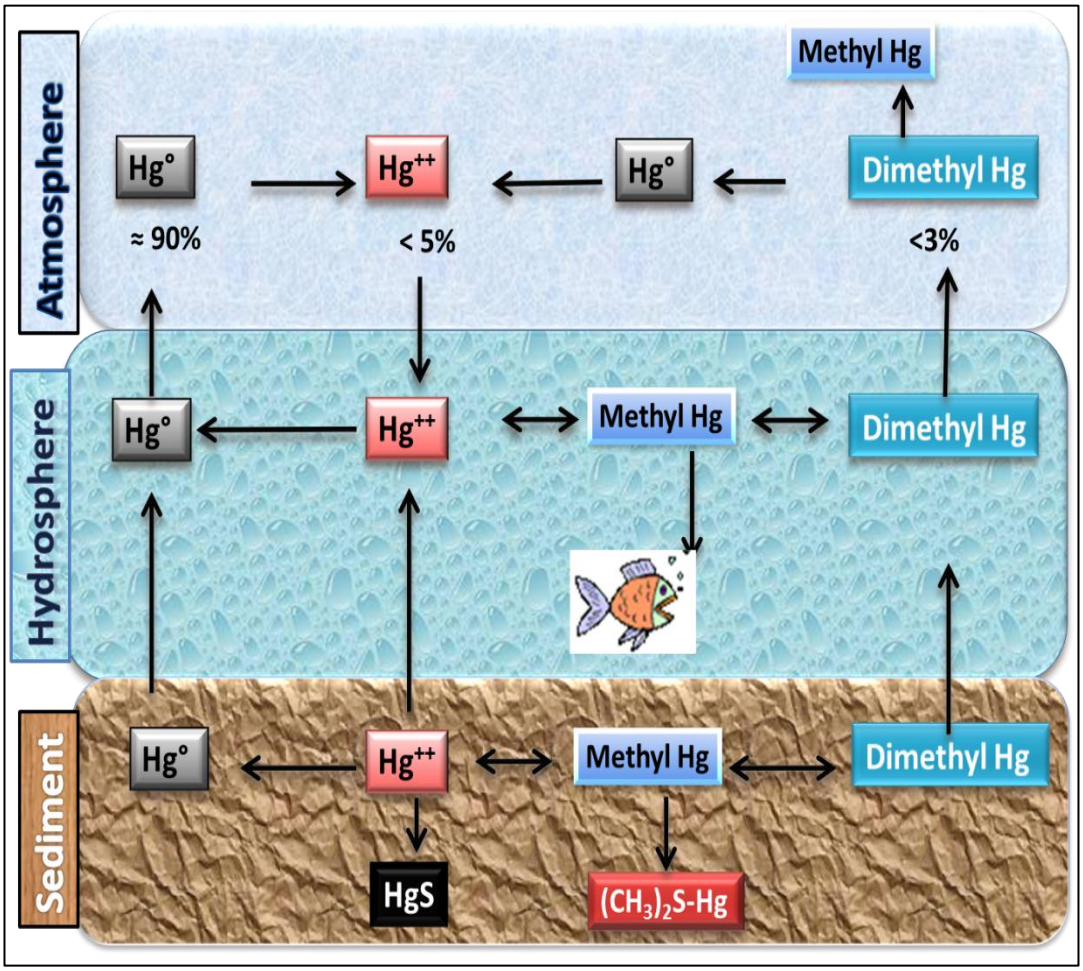


Figure 1.2 Biogeochemical cycle of mercury in the environment

K. Lepold in his analytical review methods reported the typical mercury content and species in uncontaminated natural waters Table 1.2 [30]. Chen and co-workers [31] optimized the cloud point extraction methodology and the reverse-phase HPLC with inductively coupled plasma mass spectrometry (ICP-MS) detector to measure ultra-low levels of organic and inorganic mercury compounds, extracted from biological and environmental samples. Optimization of these techniques resulted in very low detection limits of 13, 8, and 6 ng/L for methyl-Hg^{+}, phenyl-Hg^{+}, and Hg^{+2}, respectively. Application of CPE-HPLC-ICP-MS lowered the detection limit of at least an order of magnitude compared to HPLC-IPC-MS alone. Authors noted a partial decomposition of ethyl-Hg^{+} during the extraction process; thus this methodology is not suitable for this species.

Table 1.2 Typical total Hg concentration ranges and fractions of different dissolved mercury species in uncontaminated natural waters

Water	Total, Hg (ng/l)	Fraction of Hg Species (% of total mercury)			
		Hg	Hg^{++}	Methyl-Hg	Dimethyl-Hg
Open ocean, Atlantic	0.2–3.24	10–50	30–60	<1–10	<1.7
Open ocean, Pacific	0.03–1.38	10–50	n/a	<1–10	n/a
Mediterranean Sea	0.05–1.8	6–54	9–58	10–30	<0.3
Black Sea	0.36–2.37	3–17	n/a	<1–15	<0.05–0.5
Estuarine and coastal waters	0.1–35	10–30	70–90	n/a	n/a
River	1.0–5.0	10–30	40–60	<40	n.d.
Lake	0.2–80	10–30	40–60	<40	n.d.
Rain	5.0–90	n/a	n/a	3–10	n/a
Ground water	0.1–16	n/a		n/a	n/a

An extensive literature review, up to year 2004, for gas chromatographic techniques combined with plasma spectrometry techniques applied in analysis of pollutants was compiled [32]. Mercury element represents majority of published papers due to its impact on the environment and processing technologies. Various types of spectrometers and, interfaces and types of plasma were discussed in this review. Samples were analyzed directly or in combination with derivatization techniques. Advantages and disadvantages of various technologies and their combinations were analyzed in this review.

Emteborg and co-workers [33] investigated errors introduced during derivatization of mercury species with different Grignard reagents and influence of this preparation methodology on the mercury species analysis by gas chromatography coupled with microwave-induced plasma atomic emission (MIP-AES). Butylating agent caused formation of butyl derivatives that eluted very closely with alkylated mercury peak causing increase in the background. Grignard reagents with larger alkyl groups (pentyl- and hexyl-) were found not suitable for derivatization due to poor stability of derivatized mercury compounds. Contamination with the chromatographic inlet and the chromatographic column with halides (iodine and bromine) interfered with the detection of alkyl mercury compounds through formation of organomercury halides.

Recent, 2009, extensive review of non-chromatographic methods applied in mercury analysis summarizes alternative methodologies that allow cost-

effective and simple measurement of total mercury concentration [34]. Most of the literature in this review covers food and environmental analyses. Various extractions, derivatization, trapping techniques combined with atomic spectrometry methods are compared. Information on individual mercury species is limited.

Analysis of mono-methyl mercury, inorganic mercury (Hg^{+2}) and total mercury in biological samples is discussed in reference [35]. Authors developed aqueous phase derivatization method converting mercury species to ethyl, methylethyl, and diethyl derivatives. These derivatives can be conveniently analyzed by gas chromatography with cold vapor atomic fluorescence spectrometry (CV-AFS). Total mercury concentration agreed well with the sum of concentration for individual species. Extreme care was applied in maintaining freshness of the glassware and other components. The detection limit of mono-methyl mercury and inorganic mercury as mercury element was 0.6 and 1.3 pg, respectively.

Cloud point extraction combined with inductively coupled plasma/optical emission spectrometry (ICP/OEM) was applied to biological (muscle) samples [36]. Ionic mercury (Hg^{+2}) was reacted with iodide anions to form mercury tetraiodide anions and further complexed with methyl green cation. Formed hydrophobic complex was extracted by non-ionic surfactant and analyzed by ICP/OEM. Methyl mercury ions were extracted from the remaining solution by

addition of chelating agent. Although extraction of (Hg^{+2}) was 93%, extraction of methyl mercury ions was only 50%.

Stability of various mercury species during storage and sample handling presents significant problem, regardless of applied analytical methodology [37]. Mercury (II), in the form of mercury chloride, forms mercury (I) species when mercury metal is present in hydrocarbons (heptane, toluene or their mixture). This conversion occurs within a few days period. Mercury (I) compounds form colloidal suspension and can be converted to stable butyl analogs with Grignard reagent and quantified by chromatographic techniques (GC-MIP-AES or GC-MS).

Elegant et al provided detail study of chromatographic analysis of mercury species in gas condensates [38]. Authors undertook a systematic approach to eliminate artifacts from the chromatographic analysis of mercury species, analyzed suitability of the detection method, and addressed the stability of various mercury species that may affect mercury speciation and determination. Very low mercury detection limit, 0.08 pg for alkylated mercury was reported. Effect of frequently applied derivatization methods on speciation of mercury was also discussed in this paper. Authors concluded that condensates from Thailand contain over 90% mercury in Hg(0) and Hg(II) oxidation states.

Review of mercury speciation by high-performance liquid chromatography (HPLC), provided by Harrington [39] covers literature from the 1986-1999 period.

Almost all HPLC methods apply reverse phase chromatography with organic co-solvents, chelating and ion pairing agents, and buffers.

Combination of capillary electrophoresis with cold vapor atomic absorption spectrometry was reported in [40]. Capillary electrophoresis separation method performed well for charged mercury species, with detection limits of 0.04 µg/mL. This combination of separation and detection methods reported above 98% recovery of methylmercury.

Quantification of total mercury, including organic mercury, in condensates and crude oil proved successful via oxidation of low-oxidation state mercury (0 and +1), with bromine, to mercury (+2) and subsequent reduction to elemental mercury and spectrometric detection at 253.7 nm using cold vapor interface [41]. Authors claim recoveries between 93 and 98 percent for alkyl mercury species.

A detailed study of mercury distribution, in pristine and gold-mining-contaminated soils highlighted that the presence of mercury is associated with certain mineral groups (aluminum-substituted iron oxides and aluminum oxides) and soils rich in organic matter (sulfur-containing functional groups). Oxidative and reducing conditions in specific layers of soils are also correlating with the distribution of different mercury species. Mercury extraction methods were adjusted depending on the matrix [42].

Bloom analyzed mercury species in petroleum hydrocarbons by simple extraction methods, combined with CV-AFS, and investigated stability of major

mercury species (Hg^0, Hg^{+2}, CH_3HgCl, and $(CH_3)_2Hg$). The study proved that porous polyethylene containers adsorb large amounts of Hg^0 and $(CH_3)_2Hg$. Most metal containers are not suitable for sampling intended for mercury analysis. Hg^{+2} in the chloride form was readily adsorbed on the surface of the glass containers due to the presence of silanol sites. It is interesting that some stability experiments showed increase of mercury concentration followed by the initial decrease. This effect was particularly strong for aluminum containers and metallic mercury. Large fraction of total mercury exists in the particulate form. Filtration experiments proved that the size for the majority of particles is between 1 and 10 μm [43].

Chen and co-workers [44] analyzed inorganic (Hg^{+2}) and methylmercury (CH_3Hg^+) by cloud point extraction followed by HPLC separation coupled with the ICP-MS detector. The extraction methodology, the HPLC separation, and ICP-MS conditions were optimized in this work. Cloud point pre-concentration proved effective in measuring the concentration of mercury species, offering detection limits of 4 and 10 ng/L for Hg^{+2} and CH_3Hg^+, respectively.

Wang and co-workers studied the fate of different mercury species during coal burning process, and removal of mercury from flue gases [45]. The study concluded that most of the mercury species detected in the flue gas are in the form of mercury metal and mercury (II). Fly-ash from the combustion process contributes to accelerated mercury oxidation, acting as a catalyst. Oxidized

mercury species are easier to scrub by conventional processes. Fly-ash itself acts as adsorbing media; the higher the carbon content the higher adsorption capacity will be.

The published UOP method 938-10 “Total mercury and Mercury Species in Liquid Hydrocarbons” provides detail step-by-step methodology for analyzing total mercury [46]. This method applies two-stage gold traps to amalgamate mercury and release it to a CV-AAS or CV-AFS detector.

1.3 MERCURY REMOVAL

1.3.1 MERCURY REMOVAL FROM WATER

The World Health Organization (WHO) recommended the maximum mercury limit to be 0.001 ppm in drinking water as mentioned earlier. Also the new environmental guidelines of controlling the mercury limit in the discharge wastewater into the sewers by a maximum of 1 ppb dictated the needs of removing mercury using the appropriate methods [17-19]. There are several well developed conventional techniques to remove mercury and other heavy metals from wastewater and drinking water to the acceptable limits such as chemical precipitation, coagulation-flocculation, ion exchange, reverse osmosis, complexation-sequestration, and biological treatment [47,48]. The most widely used process for removing heavy metals from the wastewater is the chemical precipitation. The concept is to use some certain chemicals that form complexes with heavy metals leading to low solubility in solution [47,48]. Table 1.3

summarizes these methods and their efficiency of removing mercury from wastewater [48].

Table 1.3 Techniques used to remove mercury from wastewater.

Methods	Techniques	Advantages	Disadvantages	Hg removal %
Chemical precipitation	Sulfide (e.g., Sod. Sulfide, Sod. Hydro Sulfide, Magnesium Sulfide or other sulfide salts) is added to the waste stream to convert the soluble mercury to the relatively insoluble mercury sulfide form	Most effective near neutral pH, economical, water can reused, fast process	Difficulty of real time monitoring of reactor sulfide levels, generation of toxic residual sulfide sludge disposal problems.	95-99.8
Conventional coagulation	Using aluminum sulfate (alum) iron salt and lime	Good for higher Mercury concentration	Does not give desired precipitation	70-98
Adsorption by activated carbon	Activated carbon	Efficient and easy to handle, water can be reused after regeneration	Slow reaction suitable for low concentration, high regeneration cost	60-95
Adsorption by natural materials	Natural waste material are used as adsorbents	Easily available, ecofriendly. Economical, lesser secondary effluents	Slow process	80-95
Ion exchange	Various ion exchange resins are used for the removal of the mercury	Insensitive to variability, can achieve zero level contaminant, resin can reused after regeneration	Regenerated brine must be disposed, cannot typically used for water with a high total dissolve content, high setup cost	90
Reverse Osmosis	Cellulose acetate, aromatic polyamide membrane are used at very high pressure as a result of which solvent is forced out through membrane to the dilute solution	Compact process at mild temperature, simultaneous separation and concentration	Operated at high pressure can cause damage to the equipment, frequent clogging and choking, high operational and capital cost	91-93

Recently there has been some research conducted on developing sorbents that can remove organic or inorganic mercury from wastewater utilizing different materials. Aaron Hutchison et al synthesized group of ligands that can bind with mercury. This was based on the commonly known fact that the mercury can make strong complexation with other ligands in the linear or tetrahedral geometries. His work focused in making these ligands with alkyl hydrocarbon chain of three or four carbon atoms having sulfide group in both ends. This is to give better flexibility to bind with mercury in a tetrahedral shape. The results showed that the precipitation of $HgCl_2$ solution ranged from 90 to about 98% mercury removal in a ratio of ligand to mercury 1:1 [49].

M. Zabihi and his coworkers demonstrated that the powder activated carbon derived from the walnut shell has the ability to remove Hg^{++} from aqueous solution up to 90% at low pH [50].

Ridvan Say et al conducted a study on investigating the performance of ditheocarbomate-anchored polymer/organosmectite composite in removing several mercury species such as Hg^{++}, CH_3Hg^+, and $C_6H_5Hg^+$ from aqueous solution, whether separately or in a mixed solution [51]. The mercury removal was dependent on the mercury types and concentration, and the pH of the solution. The study reported that the maximum adsorbent capacities for Hg^{++} CH_3Hg^+, $C_6H_5Hg^+$ 157.3 mg/g, 214.6 mg/g and 90.3 mg/g respectively.

H.Bessbousse et al. used sorbent and filtration approach using poly(vinylalcohol)/poly(vinylimidazole) complexing membrane to remove Hg^{++}

from water. The removal of Hg(II) was more than 99.4 % when the system was used in the filtration mode using solution with mercury content of 91.6 or 17.5 mg Hg/l. The work also highlighted that the capacity of removing mercury is much less than the theoretical exchange capacity indicating that most of the internal sites of the membrane are not accessible to mercury [52].

Several studies have been conducted in using modified activated carbon with some ions for mercury removal from water. Using modified activated carbon provides several advantages such as high surface area, high adsorption capacity, and easy to regenerate. Kuang Min et al reported work on studying the silver-loaded activated carbon fiber and activated carbon fiber of adsorbing mercury under the nitrogen stream. The findings indicated that the sliver-loaded activated carbon fiber and activated carbon fiber have a saturation adsorption capacity of 192.3 mg/g and 29.4 mg/g at 70 ºC, which are 48-129 and 7-29 times of the common activated carbon respectively [53].

Jianhong Zhu et al. modified the surface of the activated carbon by introducing nitrogen-, sulfur- and Cl-containing functional groups to enhance mercury removal from aqueous solution. The mercury sorption capacity and rate by modified activated carbon was found to be better than activated carbon alone [54].

Carbon nanotube and nanofibers have been used in many applications, whether in their normal or modified forms with other functional groups and ions. Their specific characteristics such as: strong resistance to acid/basic media, high

porosity and surface area, the possibility of recovering the precious metals by burning, etc. attracted the researchers' attention to do more work on this field [55].

Samia Kosa et al. used multi-walled carbon nanotubes, modified with 8-hydroxyquinoline to remove heavy metals from aqueous solution. Although, this study focused on removing heavy metals such Cu, Pb, Zn and Cd from aqueous solution, it could give also good result of removing mercury[56].

Amjad Al-Sheik et al. work focused on studying the effect of the geometrical and oxidation of the multi-wall carbon nanotube (MWCNT) on the mercury (II) sorption process. The oxidation of the MWCNT created more functional groups such as carboxylic, phenolic and lactonic groups. These groups help increase the affinity of adsorbing mercury ions [57].

1.3.2 MERCURY REMOVAL FROM NATURAL GAS AND LIQUID HYDROCARBON

Raw natural gas comes primarily from one of three types of wells: crude oil wells, gas wells, and gas condensate wells. Natural gas that comes from crude oil wells is typically named associated gas. It is basically dissolved under high pressure in crude oil reservoir and released when it comes to the surface. Natural gas from gas wells and from condensate wells, in which there is little or no liquid oil, is termed non-associated gas. Gas wells typically produce only raw

natural gas, while gas condensate wells produce raw natural gas along with other liquid hydrocarbons. The hydrocarbons of higher than pentane are liquid at ambient conditions and are separated and sent to the hydrocarbon liquid for further processing, which is named as a gas condensate [58].

Removing mercury from natural gas and liquid hydrocarbons is driven by both environmental regulations and operational problems where the latter is considered to be the primary driving factor for developing appropriate technologies to remove/reduce mercury content in gas and liquid streams. There are several operational issues related to the mercury [59-62]. Mercury can cause severe corrosion of equipment materials, such as copper and aluminum and can lead to catastrophic failures of the heat exchangers at the gas plants. Mercury can also make contamination of valuable products from refinery streams, such as gas streams, LPG, light or heavy distillate products. Another concern of the mercury is the poisoning of catalysts in the petrochemical plants that use gas and other petroleum products as feedstock. The risk associated with handling and dealing with mercury in the operational processing systems during the plants shutdown and maintenance by the personnel is another concern.

Industrially, in the past there was a little interest in removing mercury from natural gas until an incident triggered the attention to address the need of removing it. The incident happened in Algeria in the early 1970s where catastrophic failures of the aluminum heat exchangers as a result of mercury corrosion [59-60]. Such incidents led to the development of several technologies

that have been implemented widely to remove/reduce mercury from natural gas streams to very low acceptable limits. The new technologies are very successful in achieving the desired results of reducing mercury content in gas streams to below detectable level or less than 10 $\mu g/m^3$ (≈1 ppb). The satisfactory mercury removal performance of these technologies depends on the mercury species and content and the nature of sorbents material. Several materials used sorbents such as silver-doped in molecular sieve, sulfur-impregnated in activated carbon, metal-sulfide material impregnated in alumina or activated carbon, potassium iodide in activated carbon have been used [63-67].

Some work has been published lately on the utilization of different materials to capture mercury from gas emission. Zhang An-chao et al reported that elemental mercury can be removed from coal combustion gas using bentonite-chitosan and their modified form by iodine and sulfuric acids. Chitosan is a polyatomic polymer produced as a waste product from the seafood processing industry which is available, biodegradable and easy to modify chemically. The results of this study showed that the chitosan-iodine modified bentonite gives the highest mercury removal compared to the raw chitosan sorbent, or its iodine modified forms [68].

Another study published by Junwei et al. demonstrated that the use of V_2O_5/activated coke (AC) catalyst improves the capturing of elemental mercury from the flue gas emission, compared to the use of activated coke only. This

increase in capturing the mercury was attributed to converting the mercury metal to its oxide form by V_2O_5. The capturing of elemental mercury was improved by increasing the V_2O_5 amount and promoted by the presence of O_2 and SO_2. The efficiency of the sorbent was inhibited by the presence of H_2O [69].

Qi Wan et al studied the gaseous elemental mercury removal by hydrogen chloride over CeO_2-WO_3/TiO_2 nanocomposite in simulated coal-fired flue gas. The study indicated that about 95% of the mercury was removed in presence of O_2 at a temperature that ranges from 200-400 ºC. It was found that the water vapor slightly inhibited the removal of mercury [70]. Haidiang Wang et al used the titania nanotubes (TNTs) using photocatalytic-oxidation-adsorption behavior. The results showed that the mercury removal was more than 90% after 100 hours. The TNTs calcined at 500 ºC showed the highest mercury removal [71].

There are some developed technologies to remove mercury from liquid hydrocarbons, particularly the low boiling point range such as LPG, light naphtha, and gas condensates. These technologies have been implemented in different parts of the world as shown in Table 1.4 [72,73].

Table 1.4 Mercury removal units used at different parts of the world.

Location	Hydrocarbon	Start-up date	Hg (ppb)
UK	LPG	1997	60
Middle East	Condensate	1999	10
Middle East	Condensate	2009	50
Far East	Naphtha	2002	20
Far East	Naphtha	2002	385
UK	Naphtha	2003	100
Far East	LPG	2000	292
Netherlands	Condensate	2004	300
Australia	Condensate	2004	270
Turkey	Naphtha	2009	100

In the past, the mercury removal was based on its reactivity with elemental sulfur which is impregnated on carbon, however there are some problems associated with this approach. The sulfur can be lost by leaching in hydrocarbons and thus affect the product quality in terms of sulfur limit specification. The disposal of used sorbents is an environmental concern where mercury can be removed only by a thermal process. The sorbents can lose sulfur during the startup and commissioning as it needs to be adequately equilibrated with feed and thus reduce the sorbent efficiency [74].

Therefore, new sorbents materials were developed based on inorganic materials that are highly reactive toward mercury. The mercury or its compounds can react with sorbents' active material to form HgS, HgI or form amalgam that can be retained in the support material. The commercial sorbents that are used for mercury removal, consist of two main parts; substrate support, like zeolite, activated carbon, alumina, metal oxides, etc., and reactive constituents bonded to the support such as Ag, KI, CuS, metal sulfide, etc. Some of these technologies can be applied for removing mercury from gas and some from liquid hydrocarbons as shown in Table 1.5 [74,75].

Table 1.5 Different mercury removal systems

Reactant	Substrate	Reactant	Application
Sulfur,	Carbon, Al_2O_3	HgS	Gas
Metal sulfide,	Carbon, Al_2O_3	HgS	Gas, liquid
Iodide	Carbon	HgI_2	Dry liquid
$Pd+H_2$ -metal sulfide	Al_2O_3	HgS	Liquid
Ag	Zeolite	Ag/Hg amalgam	Gas, light liquid
Metal oxide-sulfide	Oxide	HgS	Gas, liquid

The removal of mercury from liquid hydrocarbon streams depends on several factors; the feed composition, mercury content and species, temperature, water content in the feed, etc. The sorbents performance gives high removal efficiency when the feeds consist mainly of elemental mercury and the performance drops significantly with feeds having different mercury forms such as organic mercury compounds or HgS [74-76].

So far there is no proven technology used for removing mercury from heavy hydrocarbons e.g. crude or whole gas condensate, however, Muhammad Rashed et al, reported that the installation of new technology in Terengganu gas field in Malaysia to remove mercury from gas condensate was successful. The paper highlighted that the mercury was not an issue since the startup of the gas development field in 1980s until recent years where the elemental mercury was found in vessels and piping low points of the gas production facilities. This mercury concern promoted the need to build mercury removal units to avoid any operational and health problems. The mercury removal unit is required to build pretreatment process to reduce the water content from 20,000 ppm to less than 10 ppm and remove particulates to less than 10 microns. The unit was designed to reduce mercury content from 250 ppb to less than 5 ppb [77-78].

The excellent physical and chemical properties of CNT and CNF attracted many researchers to conduct studies on utilizing them in various applications and one of them is the removal of heavy metals from water and gas. No publications have been found in the utilization of CNT or CNF in removing mercury from liquid

hydrocarbon like crude oil or gas condensate. This study is focused on utilizing CNT, CNF activated carbon (AC), fly ash (FA) and their modified forms impregnated with metals or some functional groups, to study their ability of removing mercury from hydrocarbons.

CHAPTER 2

EXPERIMENTAL WORK

2.1 MATERIAL

2.1.1 HYDROCARBONS

Condensate samples were obtained on a needed basis from the upstream production lines to ensure that the samples were fresh. Several samples were used for the mercury speciation. Samples were collected in special dark glass bottles and stored in a cold place. Samples were used immediately for the mercury removal experiments every time the mercury content was to be determined for the experiment.

2.1.2 CHEMICALS AND SOLVENTS

Zeolite and Alumina, $AgNO_3$, KI, isooctane, NaCl, and mercury standards were purchased commercially. Methyl mercury chloride was purchased from VHG Labs and mercury chloride and mercury metal were obtained from SIGMA-ALDRICH. Mercury alkyl dithiocarbamate standard bought from MBH Analytical

Ltd/CONS. Cupric nitrate , Aluminum, Ferric nitrate, Titanium isopropoxide were purchased commercially to prepare the modified forms of carbon nanotubes, nanofibers, and activated carbon and fly ash . Fly ash was brought from a local plant that uses oil as a fuel. Carbon nanotubes and carbon nanofibers were purchased from Nanostructured & Amorphous Materials, Inc. USA. The purity of CNTs and CNFs are both greater than 95%. The CNTs have an average length of few microns and an average diameter of 24 nm. CNFs used have outside and inside diameters of 200–500 nm and 1–10 nm respectively. The length of these CNTs and CNFs are 0.5-2.0μm and 10–40 μm, respectively. Activated carbon purchased from commercial sources.

2.2 SORBENTS PREPARATION

2.2.1 IMPREGNATION OF SILVER ON ZEOLITE, ALUMINA AND CARBON NANOTUBE

Silver-loaded zeolites and alumina, carbon nanotube and carbon nanofiber were prepared via incipient wetness impregnation method. A volume of 40 ml of 0.05M $AgNO_3$ solution was added to 10 g of zeolite or alumina. The mixture was stirred overnight and then was filtered and washed and kept under vacuum at 100 ^oC to allow the slurry to reach dryness by water removal. All the above-mentioned procedures were performed in the dark to avoid any effect of light. The prepared adsorbents were then calcined at 550 ^oC for 6 hrs.

2.2.2 IMPREGNATION OF KI ON ZEOLITE AND ALUMINA

20 ml of 0.01 M of KI solution was added to 5 g of zeolite or alumina stirred slowly overnight. Then the samples were filtered washed with deionized water dried and calcined at 550 ºC for 6 hrs.

2.2.3 COMMERCIAL SORBENTS

Commercial sorbents that are usually used for removing mercury from light hydrocarbons such as light naphtha or natural gas were only bought commercially for comparison purposes. Codes A, B, and C were used to label the sorbents for confidentiality purposes.

2.2.4 CNT, CNF, AC AND FA MODIFIED FORMS PREPARATION

A target of five percent of elements deposited on the CNT, CNF, FA, AC material was chosen for all experiments for consistency and better evaluation. The impregnation of the elements process was carried out by first dissolving about 0.25 g of impregnating elements into a small amount of water. About 4.75 g of CNT, CNF, AC or FA was then added to about 200 ml ethanol (enough volume for material to mix adequately during sonication). Both components were mixed and stirred for one hour and the final solution was sonincated for 1 hour. Some ethanol was added to increase the mobility of the

material if needed. The sample was filtered and rinsed with de-ionized water at least 5 times or until the filtrate turned colorless. The materials were calcinated at 350 ºC under argon environment for 3 hours.

2.2.5 FUNCTIONALIZATION OF CNT, CNF, FA WITH COOH

About 250 ml a concentrated nitric acid (69%, AnalaR grade) was added to 2 g of each of CNT, CNF and FA. The mixture was refluxed under constant agitation at 120 ^{o}C for 48 hours. After cooling, the reaction mixture is diluted with 500 ml of deionized water and then vacuum-filtered through until the pH of filtrate is similar to the deionized water. The acid modified MWCNTs, was then dried in a vacuum oven at 100 ^{o}C for 24 hours.

2.3 INSTRUMENTATIONS

Cold Vapor Atomic Florescence Spectrometry (CVAFS), Millennium Merlin PSA 10.025 was used to determine the mercury content for all of the experiments using the digestion sample preparation. ESEM and XRD/XRF were used for the material characterization. ICP-AES, Spectro Ciros CCD, Axial plasma, 27 MHz, 1400 W power and the hydride generator system were also used. XRD PANalytical X-Ray Diffractometer Model: XPert PRO was used for characterizing CNTs impregnated with sulfur. Transmission Electron Microscope, TEM JEOL JEM-1400 Images taken with bottom mounted Gatan Orius SC200 CCD camera

EDS analysis with Oxford 30mm2 Si(Li) detector was used to characterize the developed sorbents. ESEM XL30 type microscope with EDS X-ray microanalyzer was used to obtain the sorbents images and elemental analysis.

2.4 VALIDATION OF THE MERCURY DETERMINATION METHOD

Two sample pretreatment approaches were used to evaluate the suitable sample preparation for accurate mercury measurements: the wet extraction and digestion approaches. ICP-AES system was used for comparison purposes.

2.4.1 SPIKED CONDENSATE WITH Hg

A condensate sample that has no detectable mercury (was tested for mercury and showed now mercury content) was used to prepare the spiked condensate with mercury. Then, one liter of this condensate, with a total weight of 748 g, was spiked by 25g of a mercury standard (100 ug/g mercury alkyldithiocarbamate standard), giving the final concentration of 3.234 ppm (3234 ppb). Then, the spiked sample was mixed and homogenized for around 30 minutes and immediately 40 samples were taken in glass vials with Teflon lined caps and kept in the cold storage. Ten samples were taken in at different dates, five were digested in Aqua regia and five samples were extracted by KBr in 500 ml Conc. HCl and/ KBrO3. Five batches were run on different days to see if there is any significant difference of the results with time.

2.4.2 WET EXTRACTION

The oxidation solution was prepared by dissolving 5.4 g of KBr in 500 ml concentrated HCl and slowly adding 7.6 g $KBrO_3$ while stirring. The condensate samples were prepared accurately by taking 3.6 g in glass vials with Teflon lined-caps. Then, 10 ml of BrCl/HCl oxidation solution was added to each sample bottle. The bottles were immediately capped and agitated in a shaker for 30 minutes prior to the extraction process. The samples were allowed to settle, or centrifuged, if needed, for 15 minutes at 3000 rpm to separate organic and aqueous layers. If the aqueous layer phase changed from orange to colorless or pale yellow, this indicates that all of the oxidizing power of BrCl was consumed. Before analyzing, the samples were filtered or pipetted off and the oil layer separated and discarded. The extracts were diluted to 50 ml and analyzed for mercury by Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS). A blank sample was also prepared in the same manner.

2.4.3 ACID DIGESTION

Condensate spiked samples were placed on a shaker for at least 2 hours, and sonicated for 15 minutes. About 1 mg of each sample was transferred to a clean acid-washed reflux digestion tube containing 10 ml of aqua regia. After agitation, the samples were then heated to 120 ºC for 1 hour. Once the samples are cooled, an aliquot of the aqueous phase was removed, diluted and analyzed directly by CV-AFS.

2.4.4 MERCURY DETERMINATION IN ACTUAL CONDENSATE SAMPLE

The freshly collected condensate samples were analyzed by two different techniques: cold vapor atomic florescence spectrometry CVAFS and inductively coupled plasma-Atomic Emission Detector (ICP-AES). In the case of the CVAFS, the sample was prepared by the digestion and extraction approaches for comparison. 10 samples were taken from the fresh gas condensate and placed in glass vials with Teflon lined-caps. Five samples were prepared by the digestion approach and run by CVAFS. Five samples were prepared by extraction approach and run by both CVAFS and ICP-AES.

2.5 MERCURY SPECIATION

UOP938-10 “Total Mercury and Mercury Species in Liquid Hydrocarbons” was used to determine the mercury species in gas condensate. This method is based on the separation and determination of soluble mercury species in hydrocarbon in term of elemental mercury, organic and inorganic mercury and ionic inorganic and organic compounds. It was proposed to cover samples containing 15 to 4000 ng/l mercury.

2.6 MODEL COMPOUNDS PREPARATION

Four mercury model compounds were prepared using different standards covering organic, inorganic and pure metal. Model 1 was prepared by adding 0.0134 g of 99.999% mercury chloride to 733 g of gas condensate. Model 2 was prepared by adding 0.164 g of 1000 ppm methyl mercury chloride standard to 738 g of gas condensate. Model 3 was prepared by adding 1.5 g of 100 ppm mercury alkyldithiocarbamate standard to 744 g of gas condensate. Model 4 was prepared by adding 0.05 g of 99.9999% of mercury metal to 748 g of gas condensate. All of these prepared model compounds were tested for mercury content and kept in the refrigerator. These model compounds were used to evaluate the mercury sorbents performance. Five ml from each model compound was used for each mercury removal experiment run. These model compounds were used also to evaluate the speciation method.

2.7 FACTORS AFFECT SORBENTS MERCURY REMOVAL PERFORMANCE

2.7.1 CONTACT TIME EFFECT

A volume of five ml of gas condensate was added to 0.1 g of each sorbent material except CNFs material where less weight of 0.05 g was used. The samples were placed in a shaker at 200 rpm for different times, 10, 20, 30, 40, 50, 60, 80 minutes. Then, about one gram of each sample was filtered and run for mercury determination. All samples were filtered using syringes equipped with a disposable filter of 0.45 μm to avoid any cross contamination or sample loss. The condensate sample was run in the same manner with every experiment for consistency.

2.7.2 MIXING RATE EFFECT

The same steps used in the shaking time experiment were used also to study the effect of shaking speed (mixing rate) at 100, 200, and 300 rpm, using the same weight of sorbents and the same volume of gas condensate, at 40 minutes shaking time.

2.7.3 SORBENTS DOSAGE EFFECT

Five ml of mercury metal model compound was added to various weights of 0.01, 0.03, 0.05, 0.07 g of several selected sorbents. Then, the samples were placed in a shaker at 200 rpm for 40 minutes. The sample then was filtered and subjected to total mercury determination. One more experiment of sorbent was

tested for mercury removal from actual gas condensate by adding five ml of gas condensate to different weights of iron impregnated on activated carbon. The used weights are 0.01, 0.05, 0.1 and 0.2 g and then run at 200 rpm for 40 minutes. The sample then was filtered and tested for total mercury determination.

2.7.4 THE EFFECT OF BOTH DIFFERENT DOSAGE, DIFFERENT TIME AND DIFFERENT RPM

Five ml of the mercury model compound was added to various weights of 0.01, 0.03, 0.05 and 0.07 g of several selected sorbents and run at 10 and 40 minutes at 200 rpm. The same experiment was repeated and run at 40 minutes at 100 and 200 rpm. All the steps for mercury determination were the same as for the other experiments.

2.8 SORBENT PERFORMANCE TO REMOVE MERCURY FROM GAS CONDENSATE

The sorbents were tested for removing mercury from actual gas condensate by taking 0.1 g of each sorbent — except the CNFs series where only 0.05 g was used and run at 200 rpm for 40 minutes shaking time. About one gram of each sample after filtration was subjected to total mercury determination. Five ml of gas condensate was used for all experiments.

CHAPTER 3

TOTAL MERCURY CONTENT DETERMINATION

The reliability of the total mercury content determination was critical to ensure that data of good precision were obtained regularly, during the course of this study. This is to evaluate the sorbents' efficiency and capacity to remove mercury from liquid hydrocarbons. Therefore, prior to starting the sorbent performance testing and evaluation, a great effort was devoted in validating the total mercury content determination method. This chapter discusses the two sample approaches for mercury content determination. Also, two different techniques were used for mercury content determination for comparison purposes.

The common detection technique used for total mercury content determination in liquid hydrocarbons is the Cold Vapor Atomic Florescence Spectrometry (CVAFS), which was used for this work [79]. Two sample preparation approaches were evaluated to select the appropriate one for this study. The method evaluation was performed first by spiking actual gas condensate with known amounts of stable organic mercury compound standard. The gas condensate free mercury sample was spiked by adding the mercury standard to produce a final

concentration of 3234 ppb. This high concentration was chosen to examine the ability of two approaches for total mercury recovery determination on different dates.

3.1 EXTRACTION APPROACH

Table 3.1 and Figure 3.1 present the results of four batches with five samples of each set prepared by the extraction method. The repeatability of the extraction approach gave mercury recovery results ranging from 93 to 100%. The average recovery for Hg in spiked condensate was found to be 96.4%. In addition the analysis of variation (ANOVA) was used to calculate the F-test for these different sets to assist the method repeatability by comparing their means statistically. The F-test was calculated using an Excel™ program to compare the various means. Table 3.2 shows that the F-obtained (3.19) at probability percentage, p =0.05, is less than the F-critical (3.24), indicating that there is no significant difference among these results. The advantages of using this approach were realized by the short time sample analysis, a few testing steps which help to eliminate the random errors associated with each step or at least avoid introducing any possible systematic errors, and there is no need for sample heating. It suffers from low total mercury recovery and applicability for heavy materials where the emulsion was encountered during mercury measurement in crude oil. The heavy sample dilution approach can help to address this issue, but it could affect the mercury determination and recovery results. This approach also suffers from extracting mercury that may exist in solid states such as HgS.

Table 3.1. Results of mercury (ng/g) using extraction approach

	Batch no, Hg, ng/g				
Replicate	1	2	3	4	**Average**
1	3153	3070	3472	3201	
2	3009	3089	3300	3210	
3	3099	2840	3201	3249	
4	3000	*3057*	*3210*	*2805*	
5	3038	3035	3099	3207	
Average	3060	3018	3256	3134	**3117**
SD	65	102	140.0	185	**123**
%RSD	2	3	4	6	**4**
% Recovery	95	93	101	97	**96**

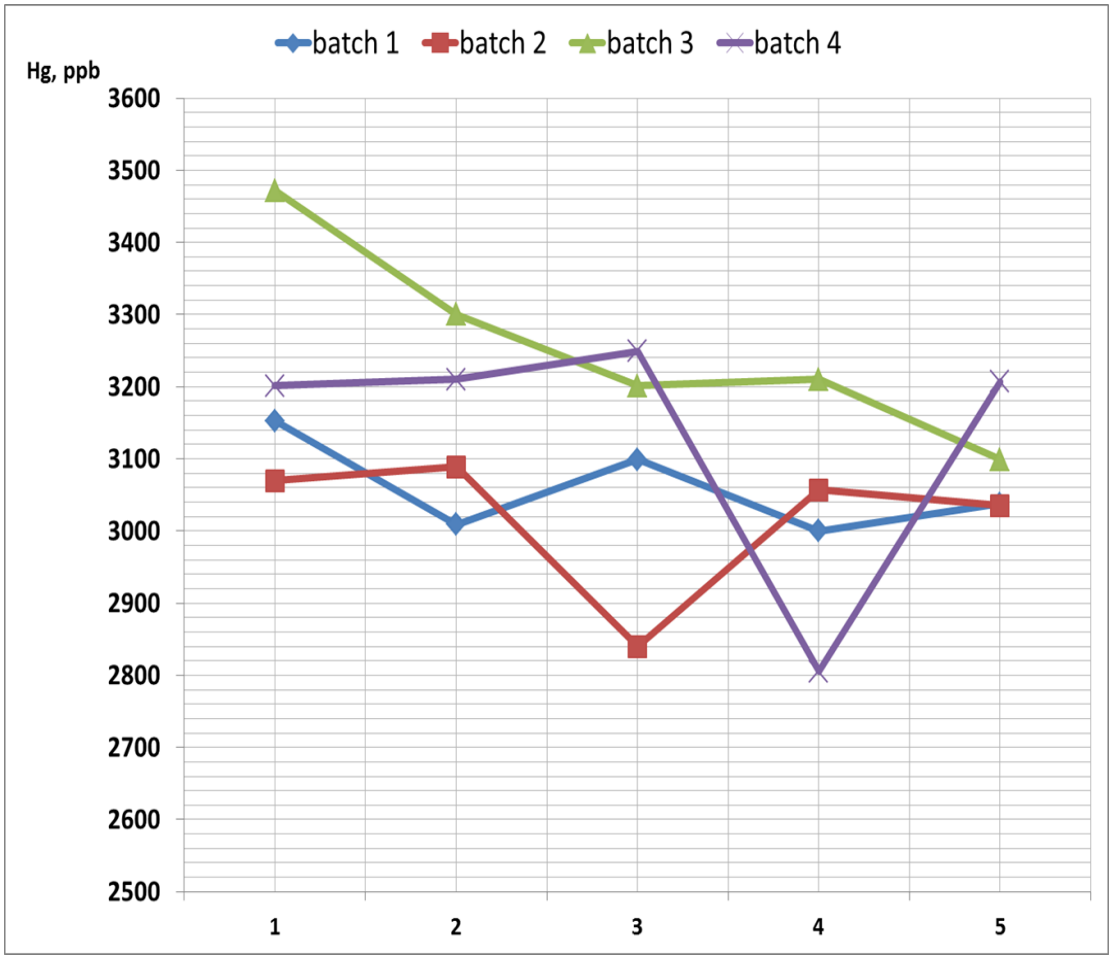


Figure 3.1 Mercury content in spiked sample by the extraction approach

Table 3.2 F-test for the extraction approach

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1	5	15299	3060	4213.7
2	5	15091	3018	10309.7
3	5	16282	3256	19595.3
4	5	15672	3134	34264.8

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	163841.2	3	54613.733	3.195	0.05	3.239
Within Groups	273534	16	17095.875			
Total	437375.2	19				

3.2. DIGESTION APPROACH

Table 3.3 and Figure 3.2 show the results of the four batches using the digestion technique. This approach showed much better mercury percentage recovery ranging from 97%- 105.9%. The average percentage recovery for all samples is about 100%. The F-test was also applied to evaluate the various means of these data sets. The calculated value of F-test (6.80 at probability percentage, p=0.05) is greater than the F-critical (3.23) indicating there is a significant difference. The average mercury recovery is about 100% of all results obtained by the digestion. In addition, the overall average of all mercury results is about 3263 ppb, which is very close to the prepared spiked sample. This gives an impression that the method is suitable for such analysis, however the statistical significant tests indicate that there is a difference. By reviewing the test method, it was found that it involves many steps that can contribute to the result variations, e.g., weighing the sample, adding other reagents such as acid, cleanness of the digestion tube, heating the samples, transferring the samples to the tests tubes, sample dilution, etc. All these steps will definitely contribute to the result variations if no precautions are taken, particularly when handling a large number of samples.

Table 3.3. Results of mercury (ng/g) using digestion approach

Batch #, Hg, ng/g					
Replicate	**1**	**2**	**3**	**4**	**Average**
1	3269	3052	3211	3168	
2	3411	3245	3317	3081	
3	3479	3300	3157	3108	
4	3515	*3154*	*3365*	*3257*	
5	3446	3020	3387	3318	
Average	3424	3154	3287	3186	**3263**
SD	95	120	97	100	**104**
%RSD	3	4	3	3	**3**
% recovery	106	98	102	99	**101**

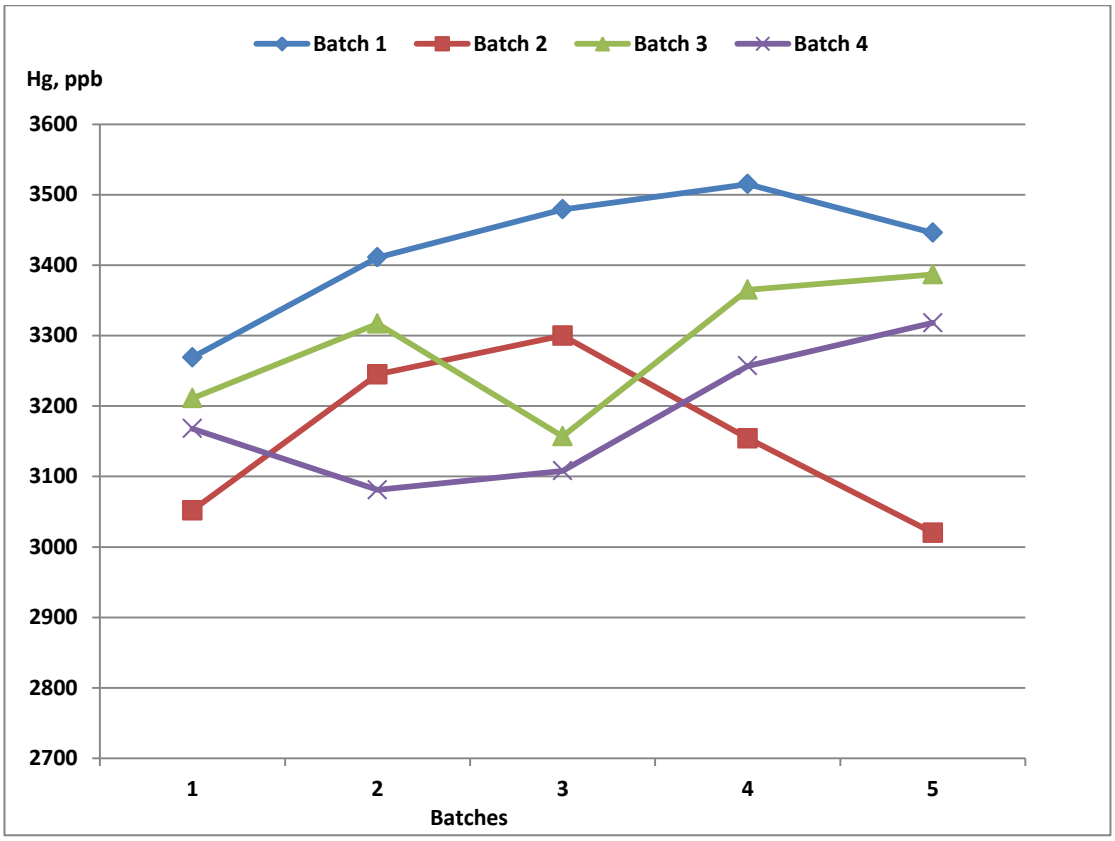


Figure 3.2. The mercury results in spiked sample by digestion approach

3.3. COMPARISON OF THE DIGESTION AND EXTRACTION APPROACHES

Two statistical tests were used to evaluate the data obtained by the two sample preparation approaches: a t-test to compare the experimental means and an F-test to compare the standard deviation by using an Excel™ program.

Table 3.4 and Figure 3.3 demonstrate the results of the extraction and digestion techniques for all samples. The average value of the digestion measurements is close to the spiked sample value and therefore it gave a better mercury result recovery than the extraction. The t-test was compared for the two experimental means of digestion and extraction, and took the null hypothesis that the two methods gave the same average results, $H_{o,}\ \overline{x}_1 = \overline{x}_2$. The observed t-value at 19 degrees of freedom is $|t| = 2.93$, which was greater than the critical value of 2.09, so that the hypothesis was rejected, and there is evidence that the two sample preparation approaches affect the mercury results, as shown in Table 3.5. The F-test shown in Table 3.6 indicated that the F calculated is 6.80, which is greater than F critical of 3.23, which indicated a significant difference between these two methods.

This difference can be attributed to both systematic and random errors generated from test procedures. In the digestion approach, there are several steps where each one generates its own error and adds to the others, finally contributing to the overall results. Systematic errors can be eliminated or reduced by ensuring that all test steps are implemented carefully, particularly in the

digestion techniques as it involves many steps. For example, in the digestion approach there are more steps than the extraction, such as sample heating and cooling, dilution, transferring the samples to the test tube, etc. These steps will be eliminated with a new introduced system that uses direct injection.

The major difference between the two approaches is noticed when comparing the prepared spiked value with average values of digestion and extraction methods. The average obtained by digestion, extraction and the value of the prepared spiked samples are 3263, 3115, and 3234 respectively. This indicates that the digestion sample preparation technique gave a close result to the spiked value, where the extraction gave a lower value. In the extraction approach there are only a few steps where the sample extracted and submitted directly to the mercury analysis.

The extraction seems to suffer from low mercury recovery, which will result in a significant difference when compared with digestion. The extraction approach is suitable for light hydrocarbons, where heavy samples such as crude oils require some dilution to avoid emulsion formation during the extraction process. It also will depend on the type of mercury species in the sample where the method is not suitable for solid mercury, such as HgS.

Table 3.4. Comparison of both sample preparation techniques (extraction and digestion)

spiked condensate (3234 ng/g)				Difference		%Recovery	
Sample #	**Extraction, Hg, ppb**	**Digestion, Hg, ppb**	**Spiked**	**Extraction**	**Digestion**	**Extraction**	**Digestion**
1	3153	3269	3234	-81.0	35.0	97.5	101.1
2	3009	3411		-225.0	177.0	93.0	105.5
3	3099	3479		-135.0	245.0	95.8	107.6
4	3000	3515		-234.0	281.0	92.8	108.7
5	3038	3446		-196.0	212.0	93.9	106.6
6	3070	3052		-164.0	-182.0	94.9	94.4
7	3089	3245		-145.0	11.0	95.5	100.3
8	2840	3300		-394.0	66.0	87.8	102.0
9	3057	3154		-177.0	-80.0	94.5	97.5
10	3035	3020		-199.0	-214.0	93.8	93.4
11	3427	3211		193.0	-23.0	106.0	99.3
12	3300	3317		66.0	83.0	102.0	102.6
13	3201	3157		-33.0	-77.0	99.0	97.6
14	3210	3365		-24.0	131.0	99.3	104.1
15	3099	3387		-135.0	153.0	95.8	104.7
16	3201	3168		-33.0	-66.0	99.0	98.0
17	3210	3081		-24.0	-153.0	99.3	95.3
18	3249	3108		15.0	-126.0	100.5	96.1
19	2805	3257		-429.0	23.0	86.7	100.7
20	3207	3318		-27.0	84.0	99.2	102.6
Average	3115	3263	3234	-119.1	29.0	96.3	100.9
SD	146	144	0	146.4	144.1	4.5	4.5
RSD%	4.7	4.4	0.0			4.7	4.4

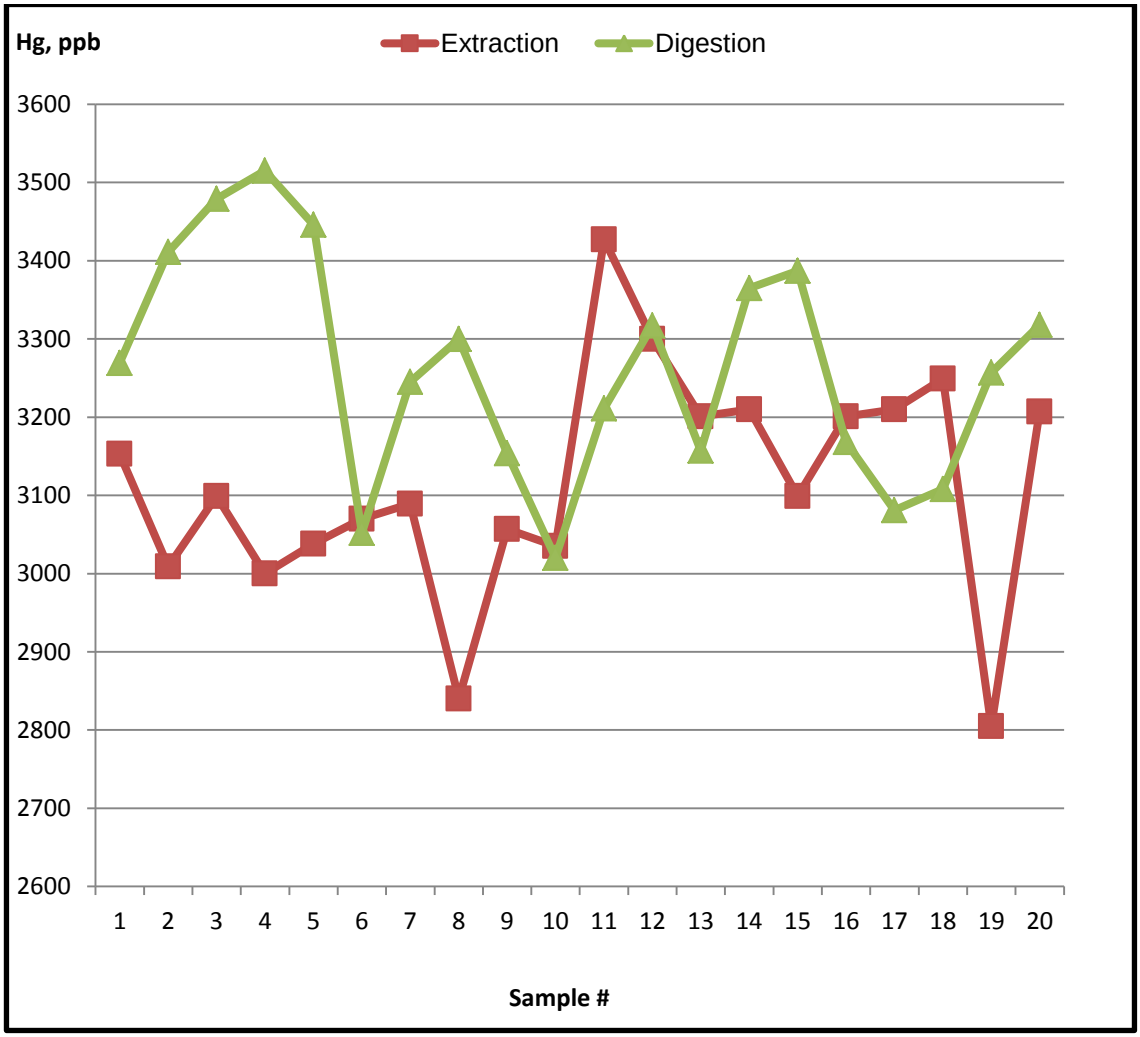


Figure 3.3. Hg results for twenty samples obtained by extraction and digestion

Table 3.5. t-test: Paired Two Sample for Means

	Extraction	*Digestion*
Mean	3114.950	3263.000
Variance	21440.366	20768.632
Observations	20.000	20.000
Pearson Correlation	-0.208	
Hypothesized Mean Difference	0.000	
df	19.000	
t Stat	-2.932	
P(T<=t) one-tail	0.004	
t Critical one-tail	1.729	
P(T<=t) two-tail	0.009	
t Critical two-tail	2.093	

Table 3.6 Single Anova Single Factor for CVAFS, digestion approach

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
1	5	17120	3424	8996
2	5	15771	3154.2	14489.2
3	5	16437	3287.4	9914.8
4	5	15932	3186.4	9974.3

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	221106.8	3	73702.267	6.797	0.0036	3.239
Within Groups	173497.2	16	10843.575			
Total	394604	19				

3.4 MERCURY DETERMINATION IN GAS CONDENSATE

Further test evaluation was conducted after taking the appropriate measures and precautions during the sample preparation steps, particularly the digestion approach, as it involve many steps. New and small digestion tubes were used, proper test tube cleaning was applied; the digestion acid was added immediately after taking the sample weight to preserve the mercury, etc. This time, the actual gas condensate and another mercury detection technique were used for better comparison and assessment. Three sets of gas condensate each had five samples subjected for total mercury determination by CVAFS, extraction and digestion and ICP-AED techniques. The average results obtained by the two different techniques were close where the ones obtained by CVAFS give higher results than the ICP-AED Table 3.7 and Figure 3.4. The F-test in Table 3.8indicates that the F-calculated (1.26) is less than the F-critical (3.89) demonstrating that there is no significant difference between the results.

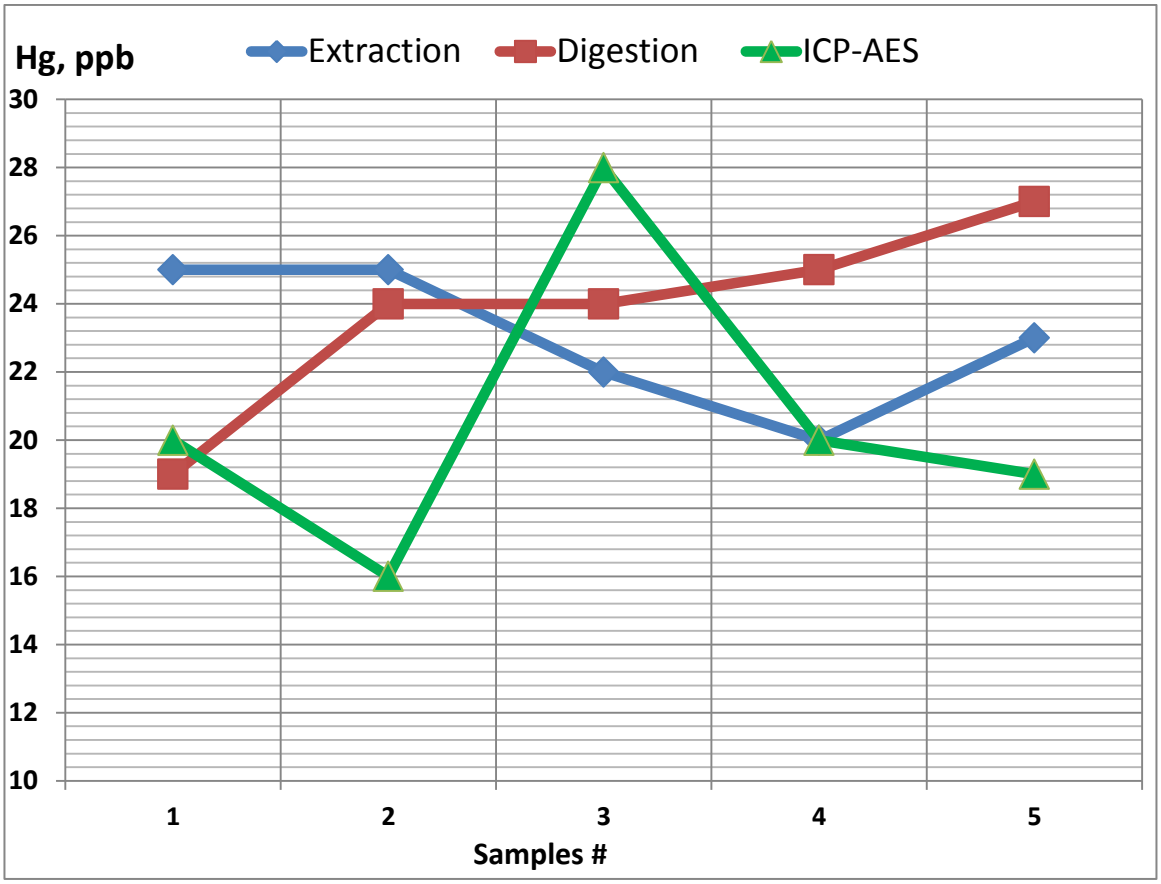


Figure 3.4. Mercury content in gas condensate using CVAFS and ICP-AES

Table 3.7. The Mercury content in gas condensate using two different methods.

Sample ID	Replicate	Mercury Results (µg/kg)		
		CVAFS		ICP-AES
		Extraction	Digestion	
Gas Condensate	1	25	19	20
	2	25	24	16
	3	22	24	28
	4	20	25	20
	5	23	27	19
Average		23	23.8	20.6
SD		2.12	2.95	4.45
RSD		9.22	12.39	21.60

Table 3.8. Anova: Single Factor of five samples Run by extraction , digestion, and ICP-AES

Groups	Count	Sum	Average	Variance		
Extraction	5	115	23	4.5		
Digestion	5	119	23.8	8.7		
ICP-AES	5	103	20.6	19.8		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit.
Between Groups	27.7	2	13.9	1.2	0.318	3.8
Within Groups	132	12	11			
Total	159.7	14				

3.5 CONCLUSION

The evaluation of the analytical method for mercury determination in gas condensate was accomplished by comparing two sample preparation approaches, digestion and extraction. Digestion approach gave better mercury recovery, but suffers from the repeatability particularly at different dates. Statistical assessment indicated that the digestion sample preparation technique showed significant difference within the same sample population or when compared with the extraction approach. Extraction approach show good repeatability, but it suffers from the low mercury recovery.

CHAPTER 4

MERCURY SPECIATION

Mercury may exist in different forms with different chemical and physical properties. Each has different characteristics in terms of solubility, volatility, toxicity, and reactivity [80]. Knowing various types of mercury chemicals species in petroleum and refining products is necessary to understand the potential negative impacts on the refinery operation, the designing of suitable materials that are resistant to mercury corrosion, or developing the mercury removal technologies.

In this study the mercury speciation in terms of organic, inorganic and free metal in gas condensate is very critical to evaluate the sorbent performance. The organic mercury speciation is very difficult task to perform due to several factors, e.g.; the low mercury level in gas condensate, the nature of the hydrocarbon matrix, and the stability of mercury compounds [81]. Therefore, the study focused on knowing the overall content of organic, inorganic and free metal in the gas condensate.

4.1 METHOD USED FOR MERCURY SPECIATION

The work was carried out using the UOP developed method UOP938–10. This method uses the concept of identifying the mercury species as free Hg^o, organic and inorganic forms; by first removing free mercury through purging the sample with helium gas for two hours, and then by adding NaCL solution to separate any inorganic mercury. The mercury content in both organic and aqueous layers was determined. The mercury of the whole condensate was also determined to calculate the mercury balance. According to this method, the mercury loss during the gas purging is mostly free mercury Hg^o with some light organic mercury compounds such as $Hg(CH_3)_2$ if it exists in the sample. The following equation was used to calculate the various mercury forms.

Free Hg = Total Hg - (inorganic Hg + Organic Hg)

The results indicate that the mercury species distribution in the same sample run at different dates, gave different results with a decreasing trend of all the mercury species, with a significant decrease in the case of free mercury Figures 4.1 and 4.2. To understand this behavior and verify whether the total mercury is decreasing with time; one identified gas condensate sample was stored in a cold place and monitored at different dates, Figure 4.3. The results clearly indicate that the total mercury content decreased with time.

One explanation may be due to the fact that most of the mercury in the gas condensate exists in volatile species (Hg^o or very light organic mercury compounds) where the mercury kept escaping from the sample during handling,

storing and testing. The second explanation is that the mercury may go under interconversion where some mercury forms can be deposited to the wall of the containers or evaporated during this process.

If the first explanation can be true, then the results of the species distribution accomplished by using the UOP method should reflect this. Meaning, all the volatile mercury species should be removed by the gas purging process during the experiments. The actual results in Figure 4.1 show that the mercury content in the organic phase did not change much compared to the Hg lost in the gas phase. It is worth mentioning that the UOP method states that the sample needs to be kept in an ice bath during the process of gas purging, and this may have some impact on the mercury results. The physical and chemical properties of gas condensate are different from one region to another, depending on the source and the geographical locations. This may limit the applicability of this method for all types of liquid hydrocarbons, particularly the cooling step.

Therefore, one sample was divided into two portions, one was run under cooling in an ice bath and one without cooling (just taken from the refrigerator) to see the impact of the cooling step on the mercury results. Table 4.1 and Figure 4.4 show the results where about 80% of the mercury was removed during the gas purging step when the sample was run without cooling; while only 15% was removed when the experiments were run in an ice bath. This gives an indication that mercury primarily exists in light organic compounds or in its pure metal form. It should be highlighted that the low mercury content, which is expected, in the

water layer is due to the fact that most of the ionic forms were already separated at the upstream operation. The gas condensate at the production facility goes under process where the gas, liquid hydrocarbon and water are separated and most of these inorganic forms, if they exist, stay in the water phase.

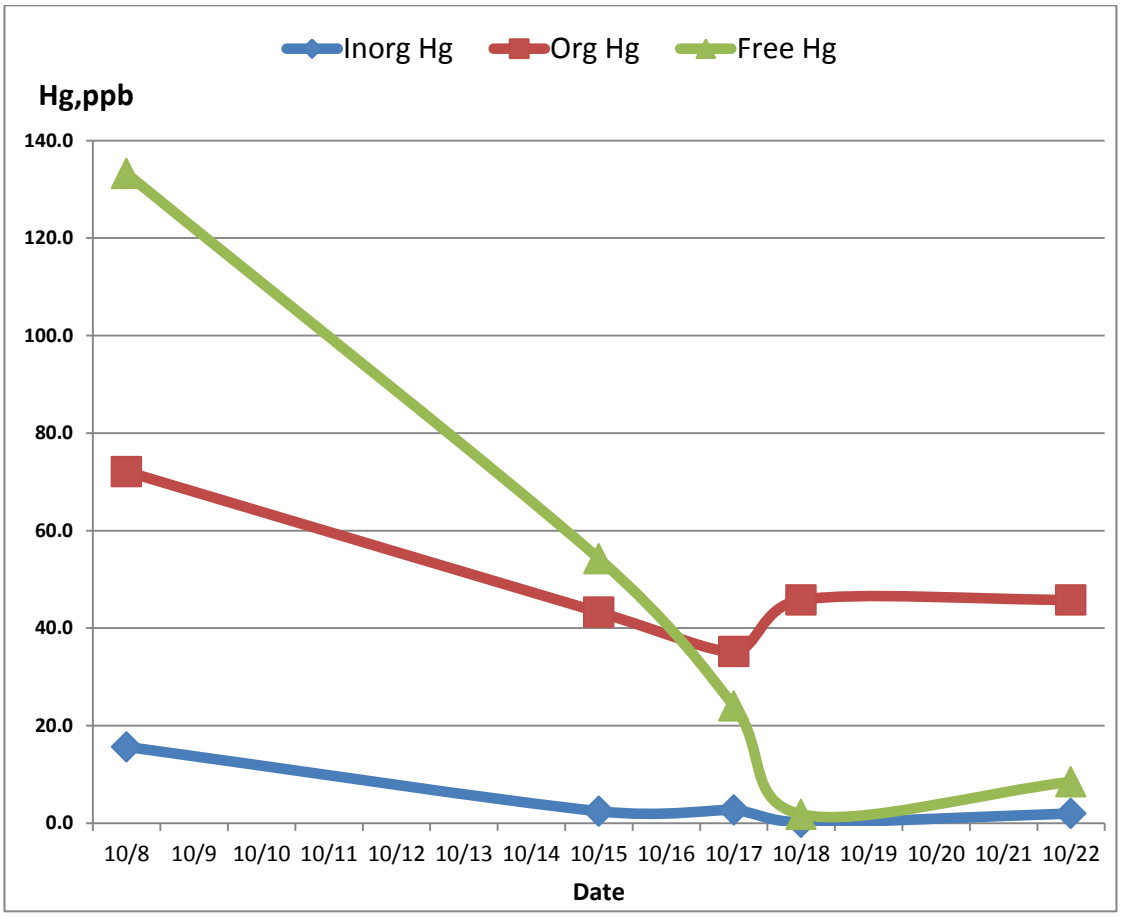


Figure 4.1 Hg species total content, ppb, distributed in gas, water and hydrocarbon layers run at different dates

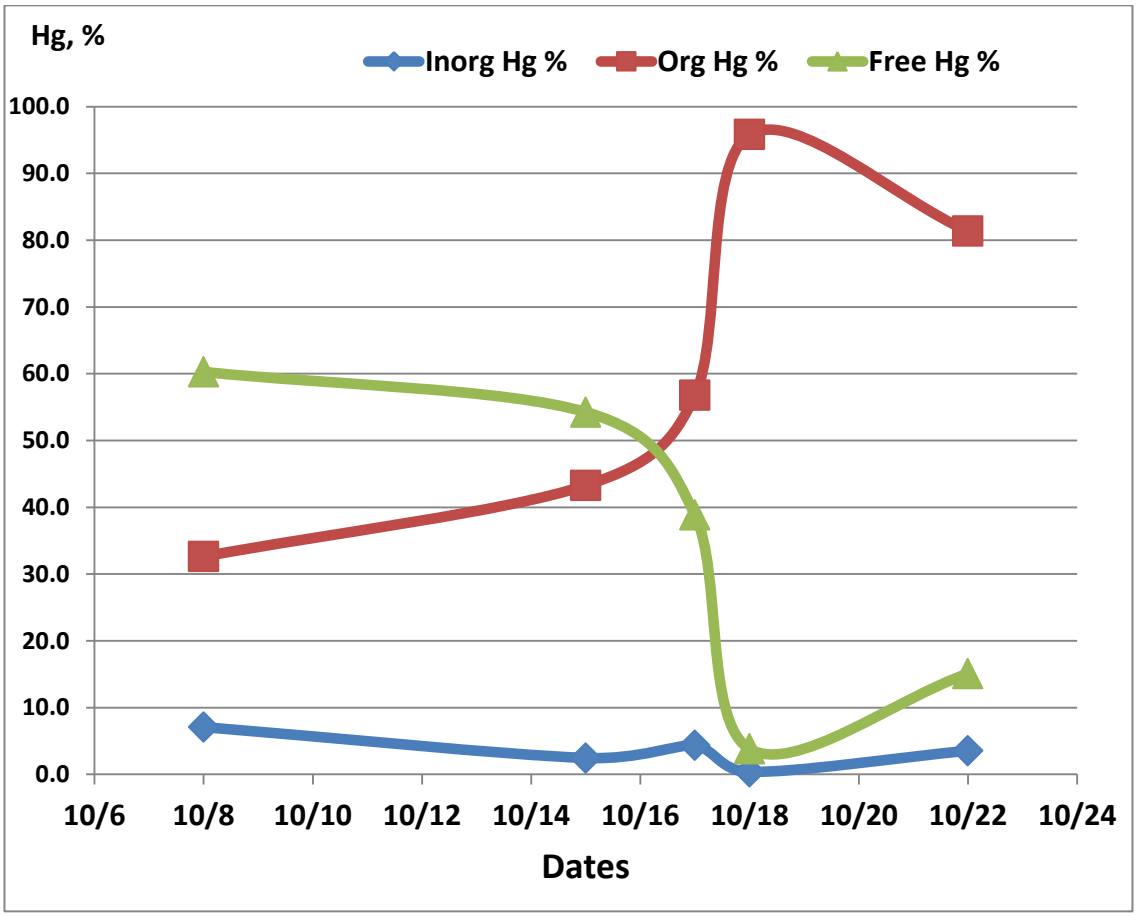


Figure 4.2. Hg percentage distributions in term of organic, inorganic, and free metal in gas, water and hydrocarbon layers run at different dates.

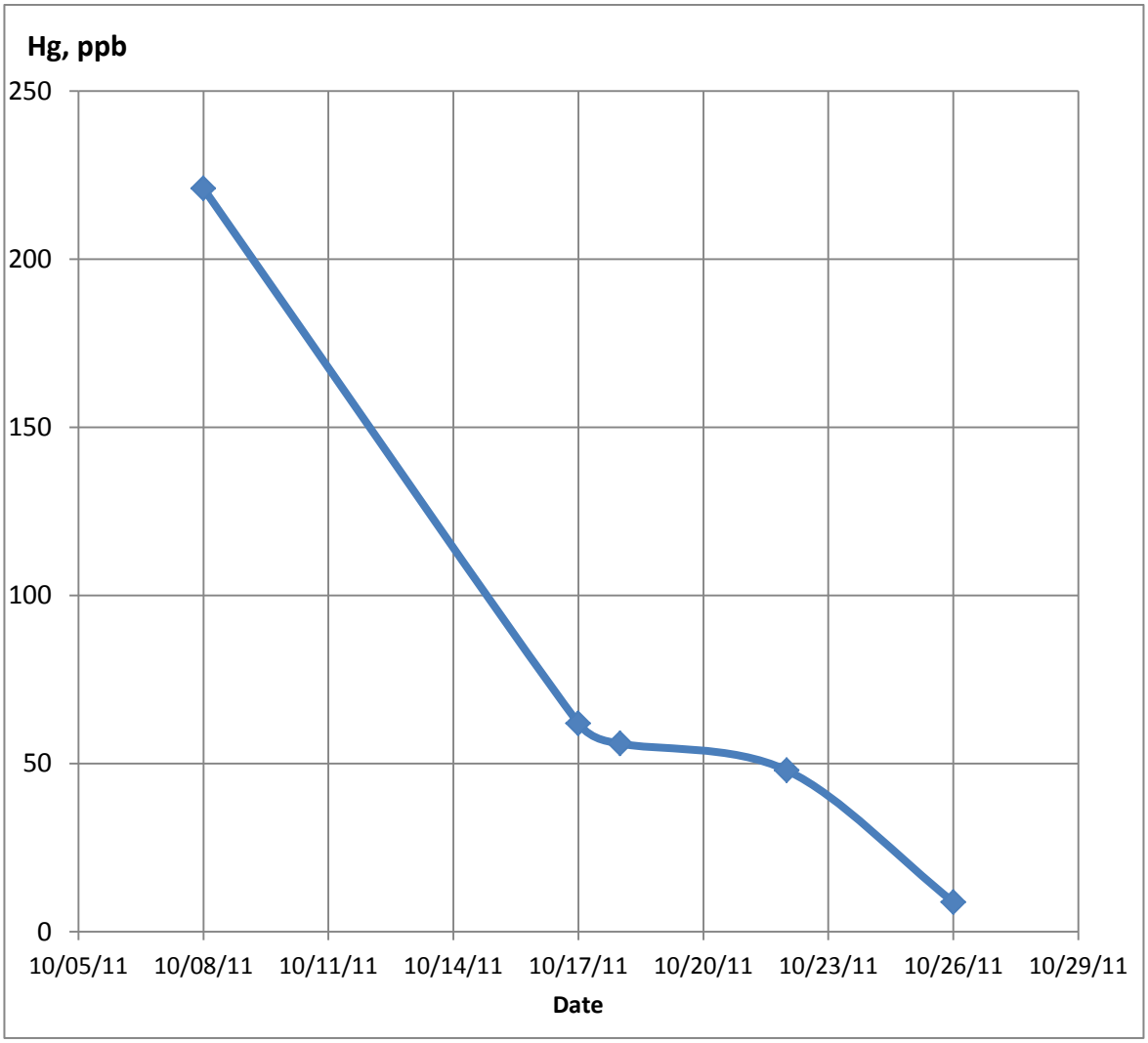


Figure 4.3. Change of total mercury content in gas condensate with time

Table 4.1 Mercury percentage distribution determined with /without cooling

Hg, %	Inorganic Hg	Organic Hg	Free Hg
% distribution ice	30	55	15
% distribution no ice	6	13	81

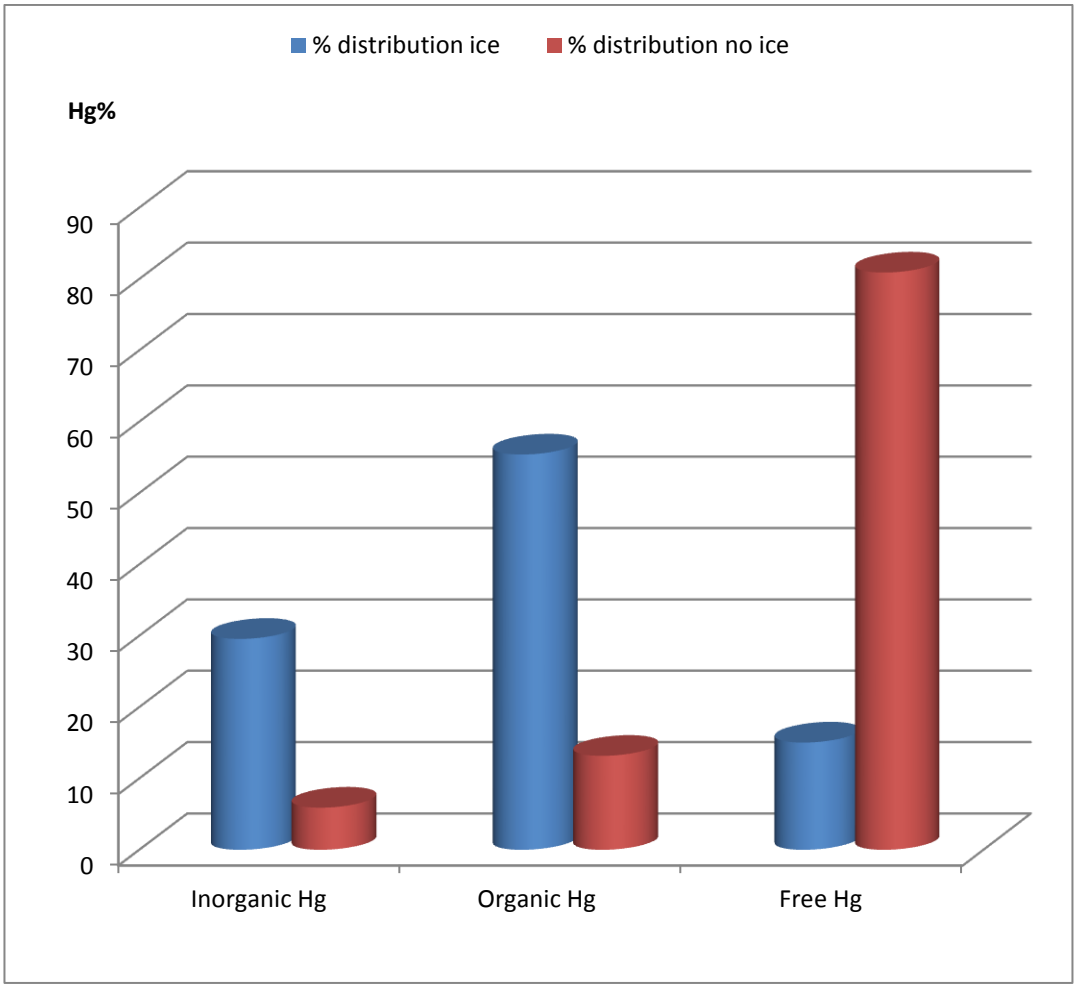


Figure 4.4. Hg percent distribution, organic, inorganic and free metal run at room temperature and in ice bath.

4.2 METHOD VALIDATION

To better assist the UOP method, different mercury model compounds prepared in gas condensate were run by this method to determine the mercury species distributions. Figure 4.5 shows the results of elemental mercury model distribution where the mercury was distributed almost equally in the organic layer and gas phase, with a negligible amount in the aqueous layer. Mercury chloride, which is expected to be mostly in the aqueous layer, was distributed by about 70% and 30% in the liquid and gas phases, respectively. This could be due to the formation of Hg complexes with some organic compounds. The Hg complexes either escaped with light hydrocarbons under the purging process or stayed in the organic layer. This is most likely true as it was noticed during the $HgCl_2$ model compound preparation step that $HgCl_2$ deposited in the bottom of the gas condensate bottle, and with time $HgCl_2$ dissolved completely.

The methylmercury chloride was distributed as expected in the gas and organic layer where about 75% in the organic layer and 25% escaped with gas flow. This also proved that some of the methyl mercury chloride can be lost during the gas purging step and could be calculated as free mercury (Hg^o) in the UOP method. Heavy mercury compound alkyl dithiocarbamate followed the same trend as methyl mercury chloride, where about 80% stayed in the organic layer and around 20% escaped with gas flow. This was not expected as the heavy organic mercury compound should stay totally in the organic phase.

It seems that the interaction of the mercury metal or its different forms with hydrocarbons makes the mercury speciation a very difficult task and therefore the need for developing better analytical tools becomes necessary.

Based on the above results all samples used were brought fresh to represent the actual mercury species for better mercury sorbents performance evaluation. In addition, the mercury content was determined for every experiment to avoid result variations.

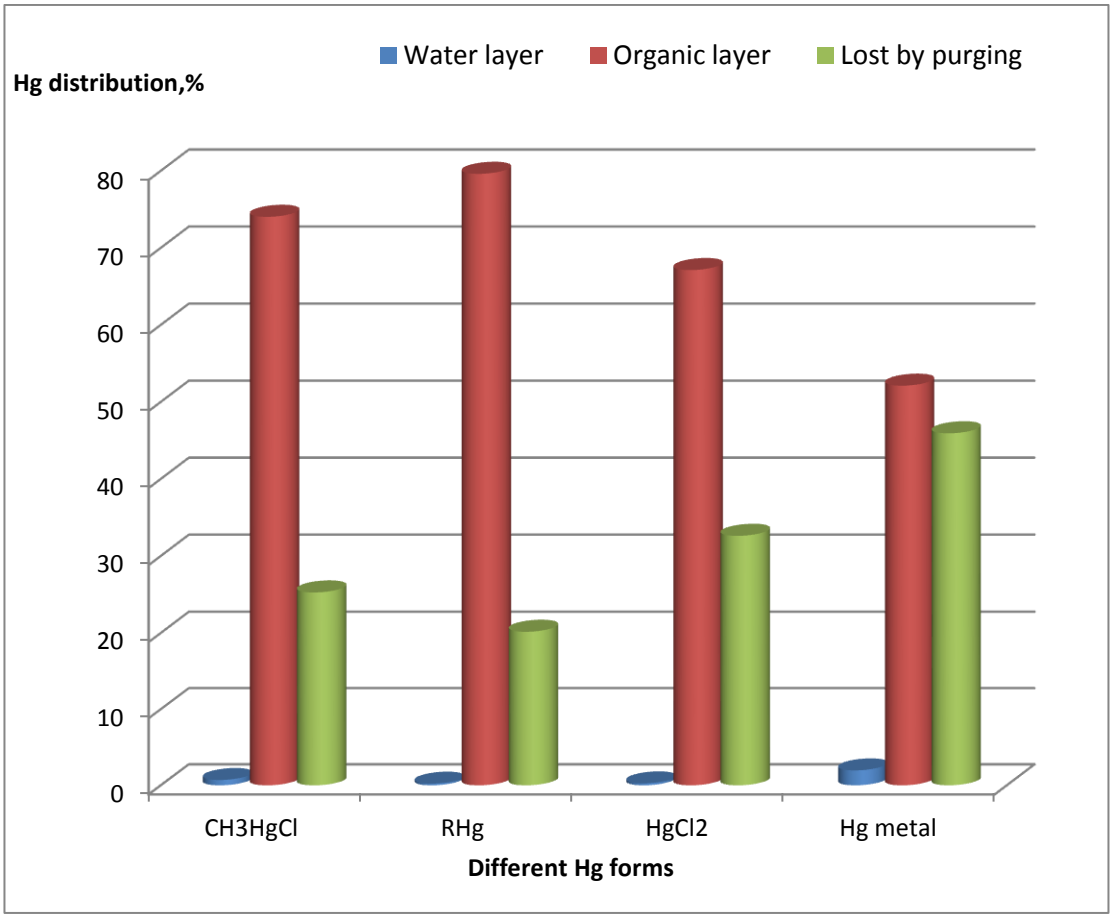


Figure 4.5. Hg percent distribution of different Hg forms in gas condensate using model compounds.

4.3 CONCLUSION

The speciation of mercury in term of organic, inorganic, and free metal was accomplished using UOP938-10 “Total Mercury and Mercury Species in Liquid Hydrocarbons in gas condensate and some mercury model compounds. The study demonstrated that mercury species as organic, inorganic and free metal could not be accurately identified due to several factors such as the gas condensate chemical and physical properties and compositions, the possibility of mercury lost, the chemical and physical interaction between mercury and hydrocarbons or interconversion process that may take place. The mercury species distribution in the same sample run at different dates, gave different results with a decreasing trend of all the mercury species, with a significant decrease in the case of free mercury. The model mercury compounds results did not reflect the expected mercury distribution in the gas, water and hydrocarbon layers indicating that mercury species behave differently when mixed with hydrocarbons. The total mercury content was also decreased with time; therefore the discrepancies in mercury results of actual gas condensate run at different labs will be seen.

CHAPTER 5

FACTORS AFFECT THE SORBENT PERFORMANCE

Selected sorbents were used to study various factors that can affect the performance of mercury removal from liquid hydrocarbons. These sorbents were used for all the experiments to study the impact of contact time, mixing rate, sorbent doses, and different mercury species on the sorbents mercury removal performance. The sorbents used are alumina-Ag, CNF-Fe, Zeolite-Ag, CNT, AC-Ti, CNF, CNT-COOH, FA –Fe and three commercial sorbents, A,B,C. The model compound of mercury metal was used to study the impact of contact time, mixing rate and sorbent dosage

5.1 CONTACT TIME EFFECT ON MERCURY REMOVAL

Figures 5.1 and 5.2 demonstrate the effect of shaking time on the sorbent mercury removal performance. In Figure 5.1 the samples were run at different time intervals at 200 rpm. The mercury removal efficiency increases with time up to 40 minutes and the performance seems to keep increasing even after 40 minutes, therefore the shaking time was increased to 80 minutes to better assist

the optimum shaking time period. The results indicate that three sorbents, commercial sorbent C, zeolite-Ag and CNF, performed well after 10 minutes shaking. All other sorbents reached the maximum mercury removal efficiency between 40 and 60 minutes, then the performance began to drop. The exceptions were commercial sorbent C, activated carbon impregnated with titanium (AC-Ti) and CNF-Fe, which reached to 98.8% 96.6 and 94.7 % receptively. The drop in the sorbents performance after 60 minutes was probably due to desorption of mercury species or its complexes. That was clearly shown in the case of zeolite impregnated with silver where the performance drops after 40 minutes. It seems that the mercury in the beginning makes Ag-Hg complex deposited on the zeolite surface and then it is desorbed into the liquid hydrocarbon where it is measured as total mercury. The other possibility is that some of hydrocarbon compounds also compete with mercury species and replace the adsorbed mercury compounds.

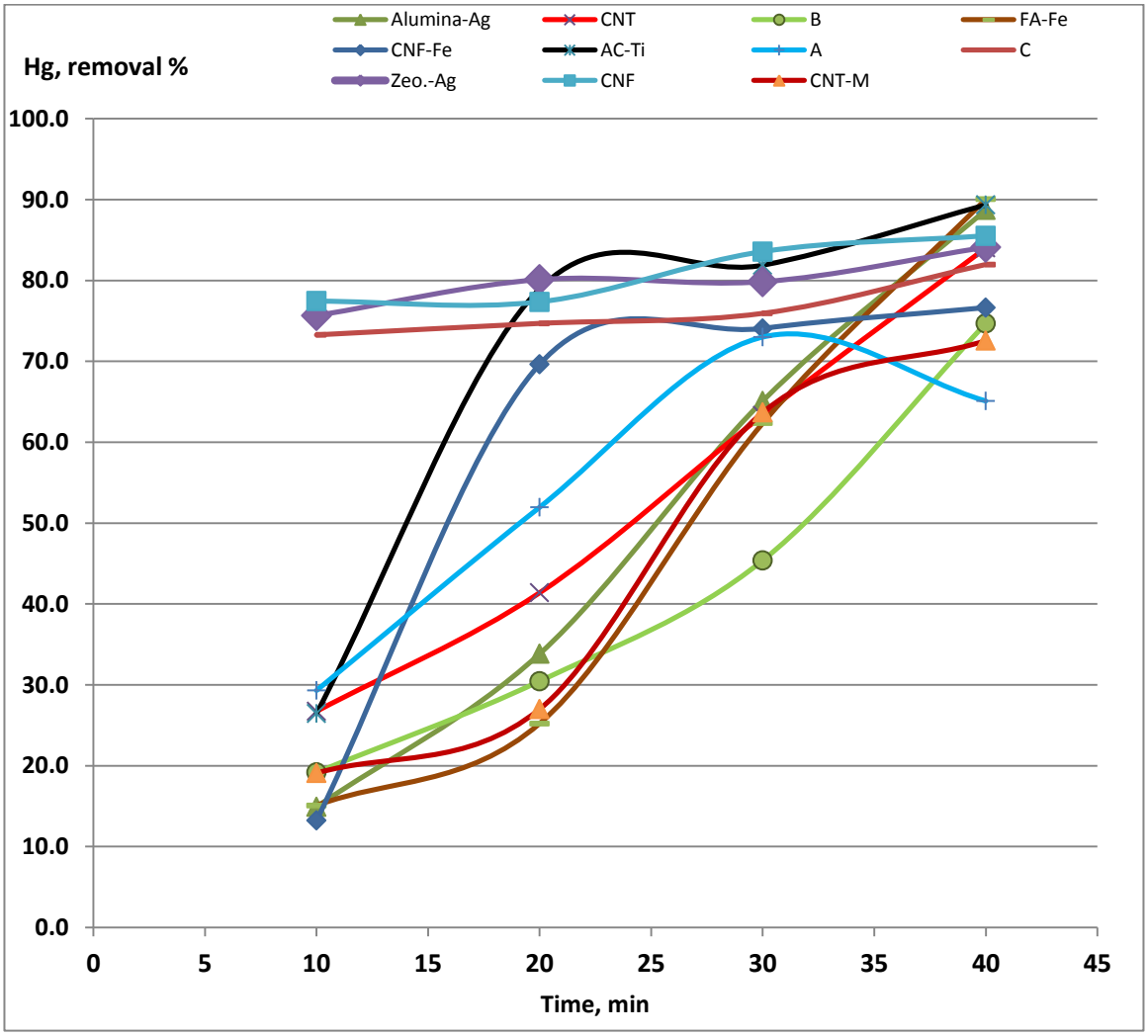


Figure 5.1. Contact time effect on sorbent mercury removal performance up to 40 minutes.

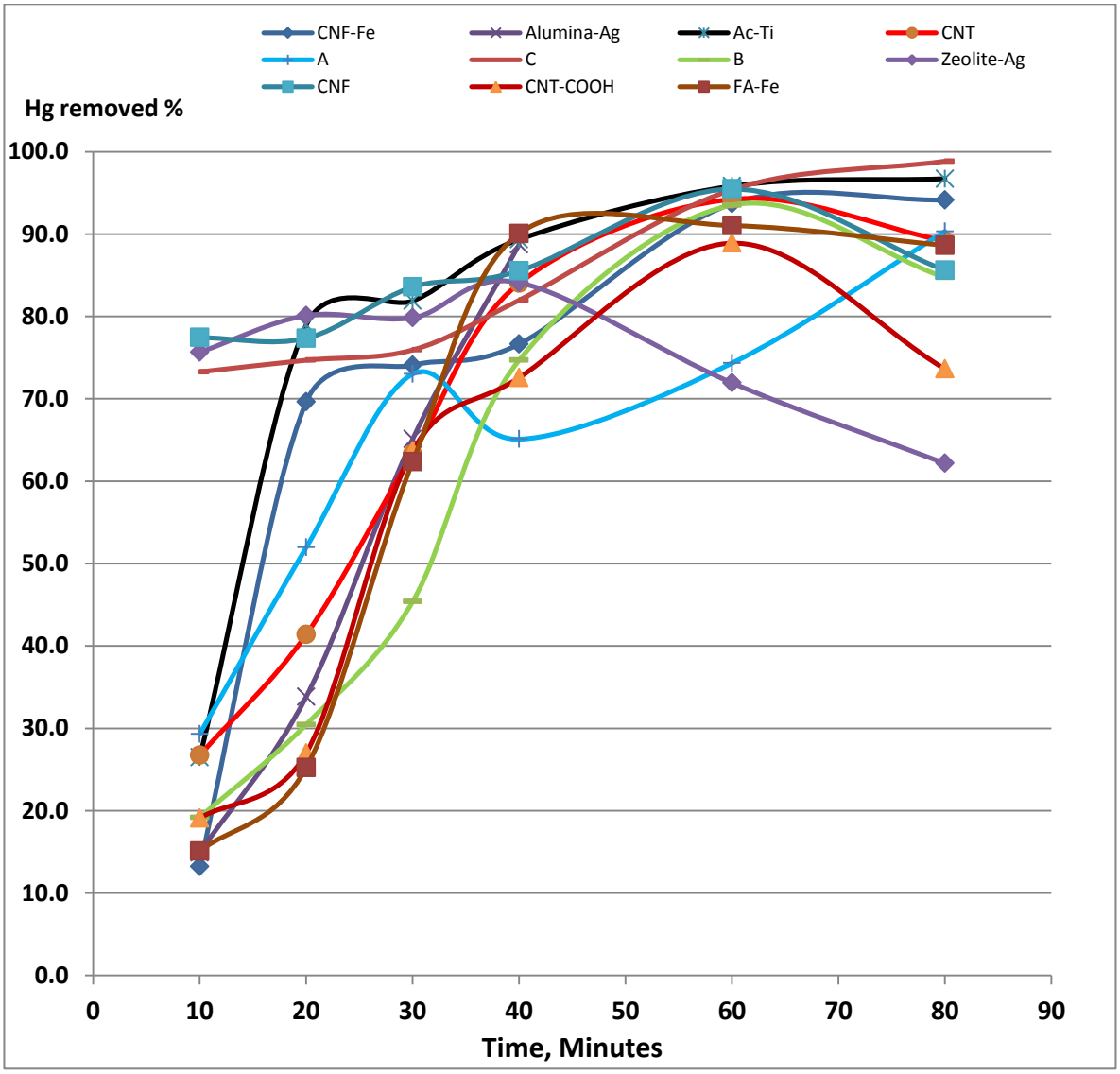


Figure 5.2. Contact time effect on sorbent mercury removal performance up to 80 minutes.

5.2 EFFECT OF MIXING RATE ON MERCURY REMOVAL

The mixing rate effect was conducted at 100, 200 and 300 rpm for several sorbents at 40 minutes contact time using fixed weight of 0.1 g for all except for CNFs series where only 0.05 g was used Figure 5.3. It was observed that the mercury removal percentage changed with different mixing rate. Overall there is a slight increase in the mercury removal efficiency with most of the sorbents tested with increasing the mixing rate from 100 to 300 rpm. Zeolite-Ag, alumina-Ag and commercial sorbent C gave the maximum removal efficiency at 200 rpm and the same performance at 100 and 300 rpm. The increase or decreases of the performance most likely is related to the sorption/desorption mechanism that take place between the mercury species and the active components of these sorbents. There are several factors affecting the sorption/desorption process such as the type of impregnated components on the support material, the surface area, the sorbent chemical structure and the composition of liquid hydrocarbons. For example carbon nanofibers (CNF) showed no significant change in the mercury removal percentage at 200 rpm and 300 rpm, while zeolite-Ag mercury removal percentage increased from around 45% at 100 rpm to about 60% at 200 rpm then dropped to 55% at 300 rpm. Overall, the mixing rate at 200 rpm seems to give better mercury removal for most of the tested sorbents.

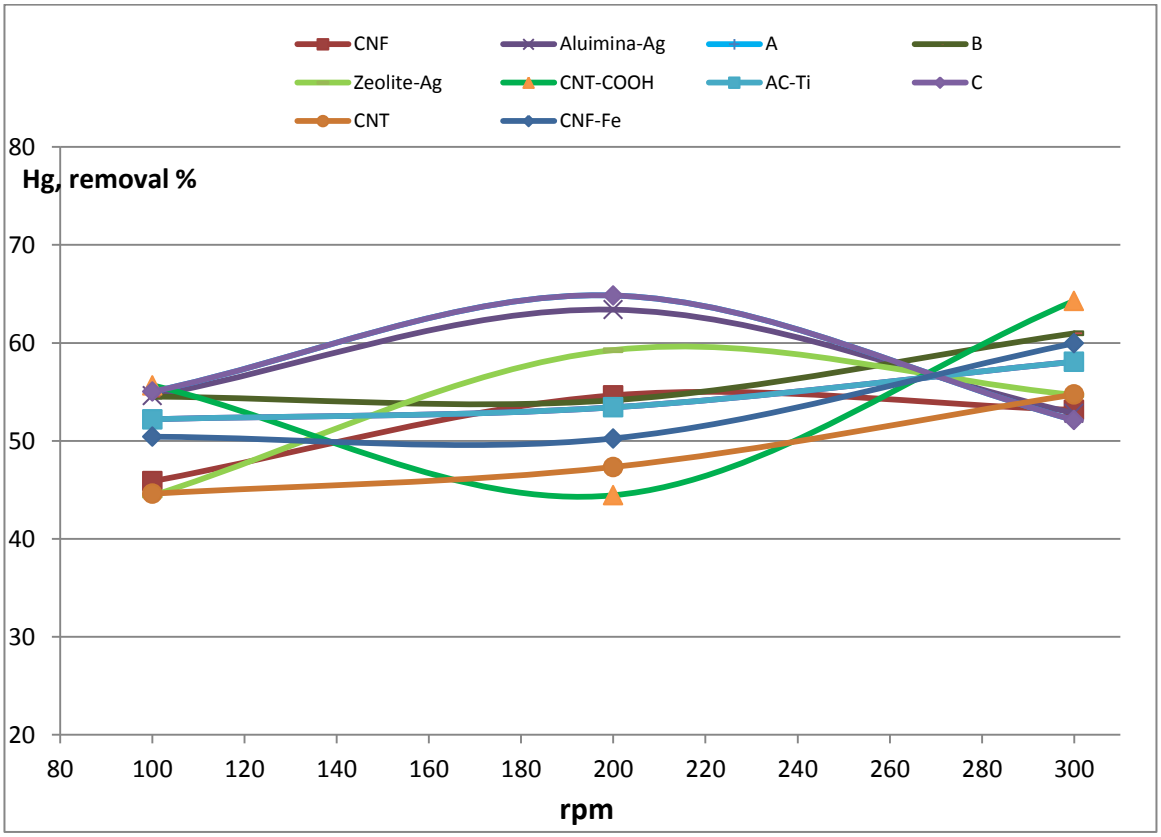


Figure 5.3. The effect of mixing rate on the mercury removal efficiency

5.3 DOSAGE EFFECT ON MERCURY REMOVAL

The mercury percentage removal is not always a good indicator of the sorbent performance. The ability to remove a high amount of mercury by using a small amount of absorbent material is the preferred option. Therefore, in addition to the mercury percentage removal, the adsorbent capacity (qe) is employed to assist the sorbent performance [83]. The mercury removal percentage is good to indicate how much mercury can be removed while adsorbent capacity gives the amount of needed sorbent, which is a good indication of its lifetime performance. The sorbent quantity and lifetime are critical for industrial applications in term of the cost and operation flexibility. The two performance indices were employed using the following equations:

$$\% \text{ Hg removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

$$\text{Adsorption Capacity, q (mg/g)} = \frac{V(C_i - C_f)}{Ws} \quad (2)$$

C_i= Hg Initial concentration

C_f = Hg final concentration

V = volume of the gas condensate (L)

W_s = weight of adsorbent (g)

Several sorbents were tested to evaluate the sorbent dosage effect on mercury removal. These sorbents were run at 40 minutes contact time and 200 rpm; there is a slight improvement of mercury removal with increasing the sorbent weights Figure 5.4. The increase of the sorbent weight from 0.01g to 0.08g gave an average removal mercury percentage for all sorbents by around 4% improvement. Some sorbents provided a pronounced increase while others did not show any significant improvement. Figure 5.5 compare the adsorbent capacity of these sorbents which follow a similar trend where increasing the sorbent weight did not provided better mercury removal. The data provided by this experiment, which was carried out in a batch setup, showed that the dosage effect has a minimum impact on mercury removal. The increase in the sorbent dosage may block part of the accessible sites of the sorbents causing less interaction between mercury and sorbent active sites. In fact, if the sorbents are designed in a bed containing different layers where the hydrocarbon can flow through, this will have better mercury removal efficiency.

One more experiment was run to evaluate the dosage effect on removing mercury. The results in Figure 5.6 indicate that the mercury removal percentage give linear relationship with increasing the sorbent weight. The overall mercury removal increased by 11% only when the sorbent weight increased by a factor of 20 (from 0.01 g to 0.2 g). Using the adsorbent capacity index, the amount of mercury removed by sorbent weight of 0.01 g and 0.2 g were 0.028 mg/g and 0.00168 mg/g respectively Table 5.1. This also confirms the previous experiment

that the increase of the sorbent weight did not provided much improvement in removing mercury at batch setup scale.

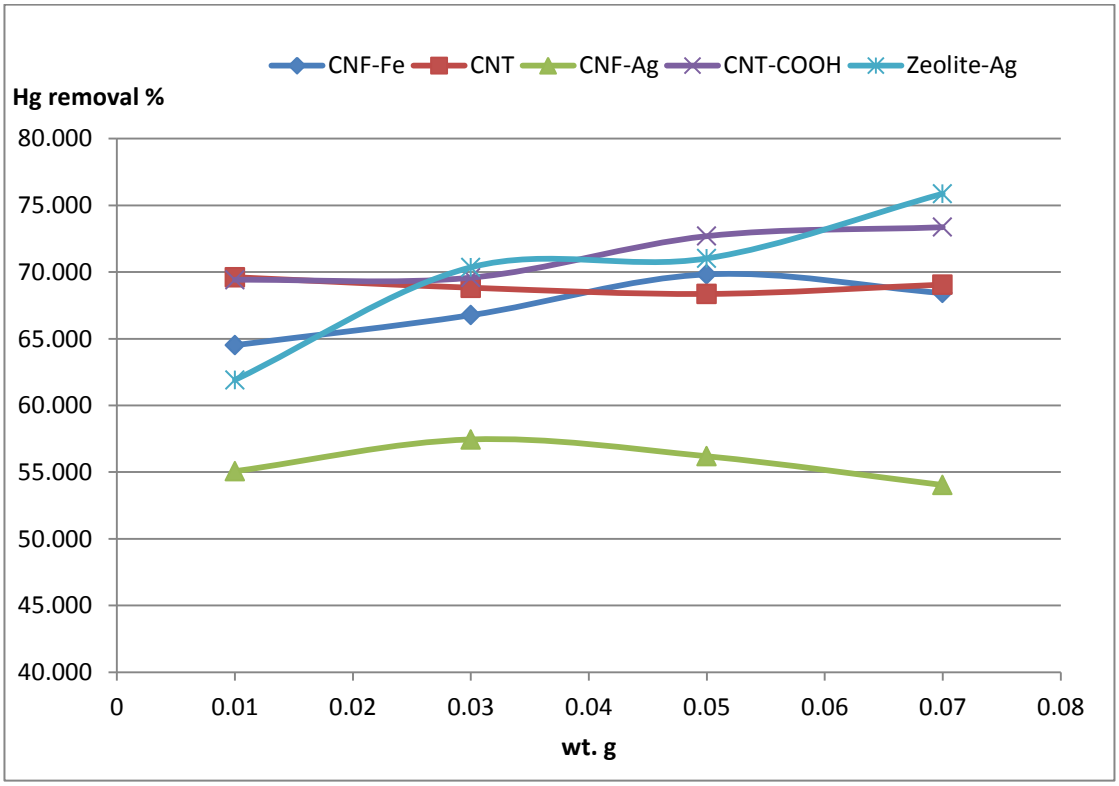


Figure 5.4. The effect of different dosages on mercury removal

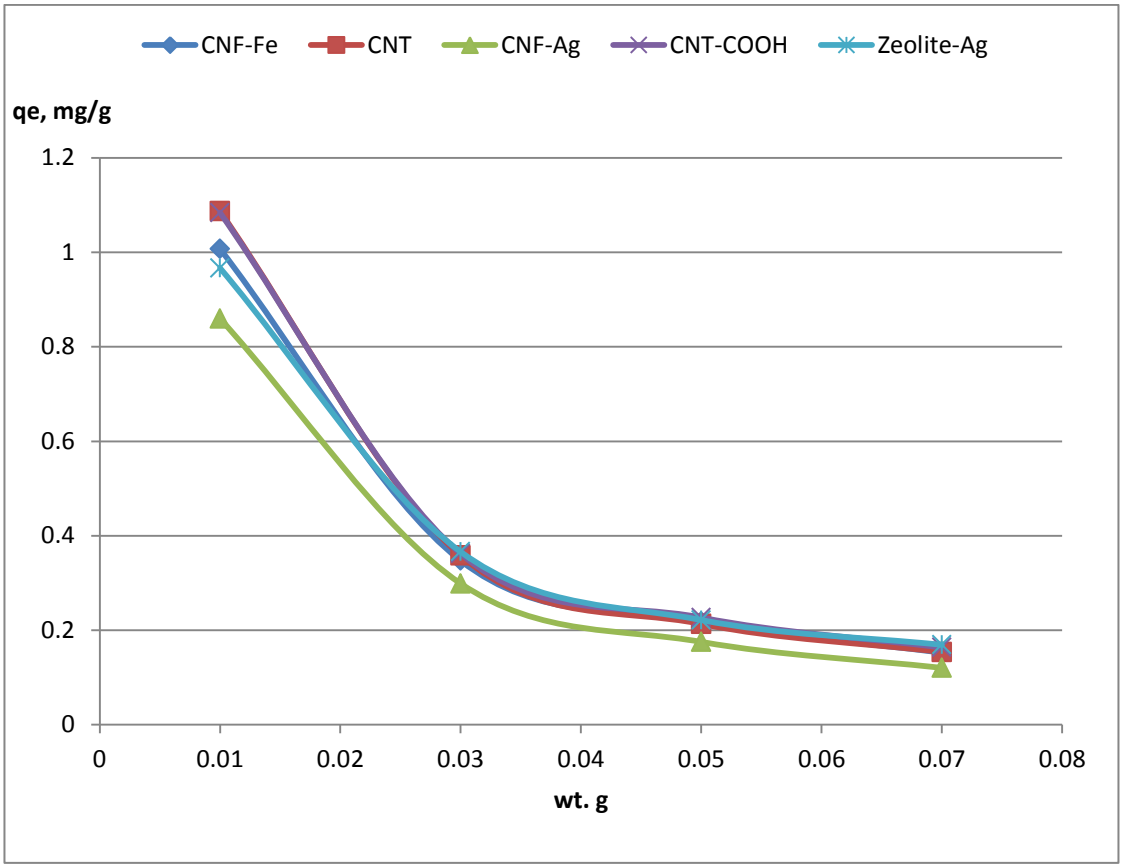


Figure 5.5. The Adsorbent capacity of different sorbents.

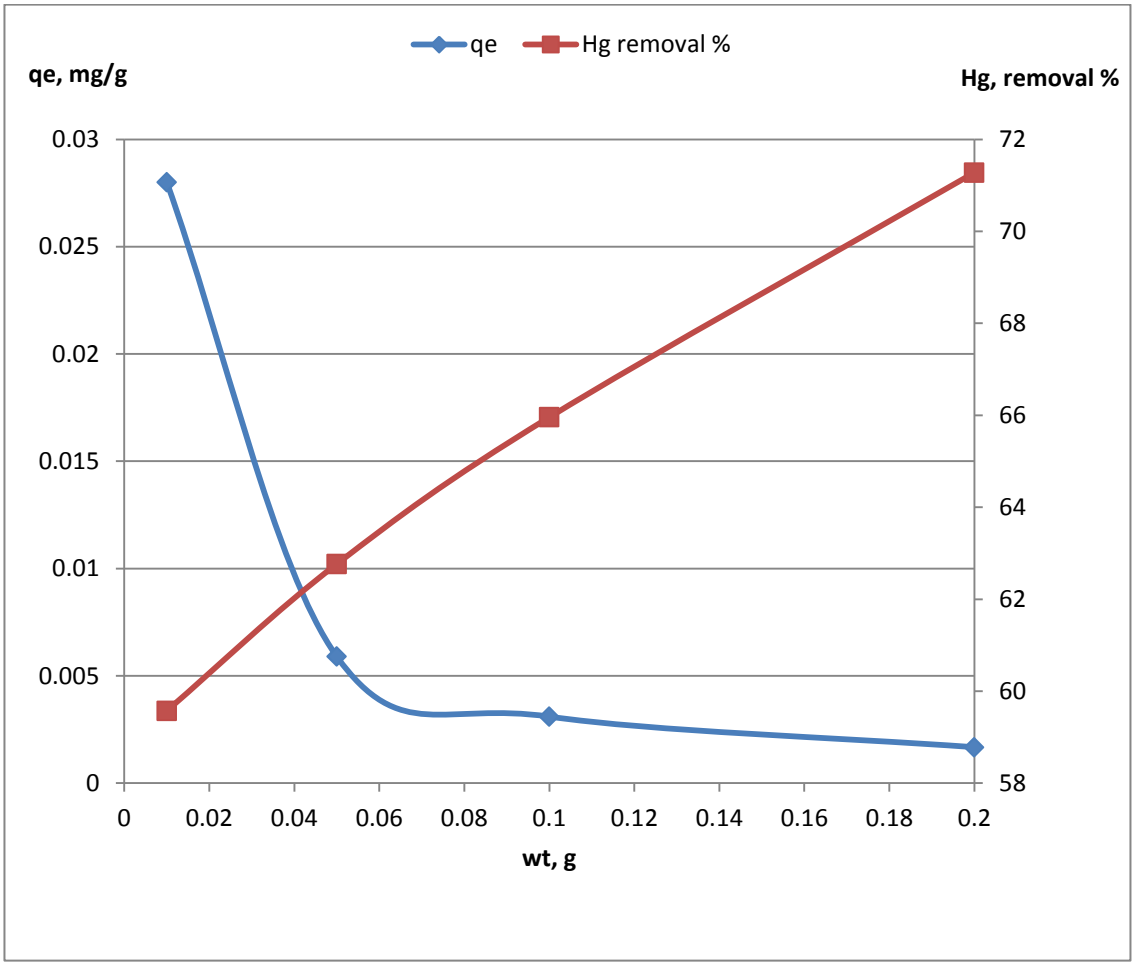


Figure 5.6. Hg removal percentage and adsorbent capacity of AC-Fe sorbent

Table 5.1. Different dosage with corresponding Hg removed, % and qe

Dosage, g	Hg removed, ppb	Hg removed, %	qe
0.01	56	60	0.028
0.05	59	63	0.0059
0.100	62	66	0.0031
0.200	67	71	0.001675

5.4 SORBENTS DOSAGE EFFECT ON MERCURY REMOVAL AT DIFFERENT TIMES AND FIXED MIXING RATE

Comparison of using various sorbent weights at two different times, 10 and 40 minutes and fixed mixing rate at 200 rpm is shown in Figure 5.7. Over all there is a small increase in the mercury removal percentage of all tested sorbents run at fixed time, but the increase is not significant. This indicates that the increase in sorbent dose at fixed mixing rate (rpm) and fixed time has minimum impact on the mercury removal efficiency. On the other hand, the effect of some sorbent dose was observed to be significant at longer contact times at a fixed mixing rate of 200 rpm.

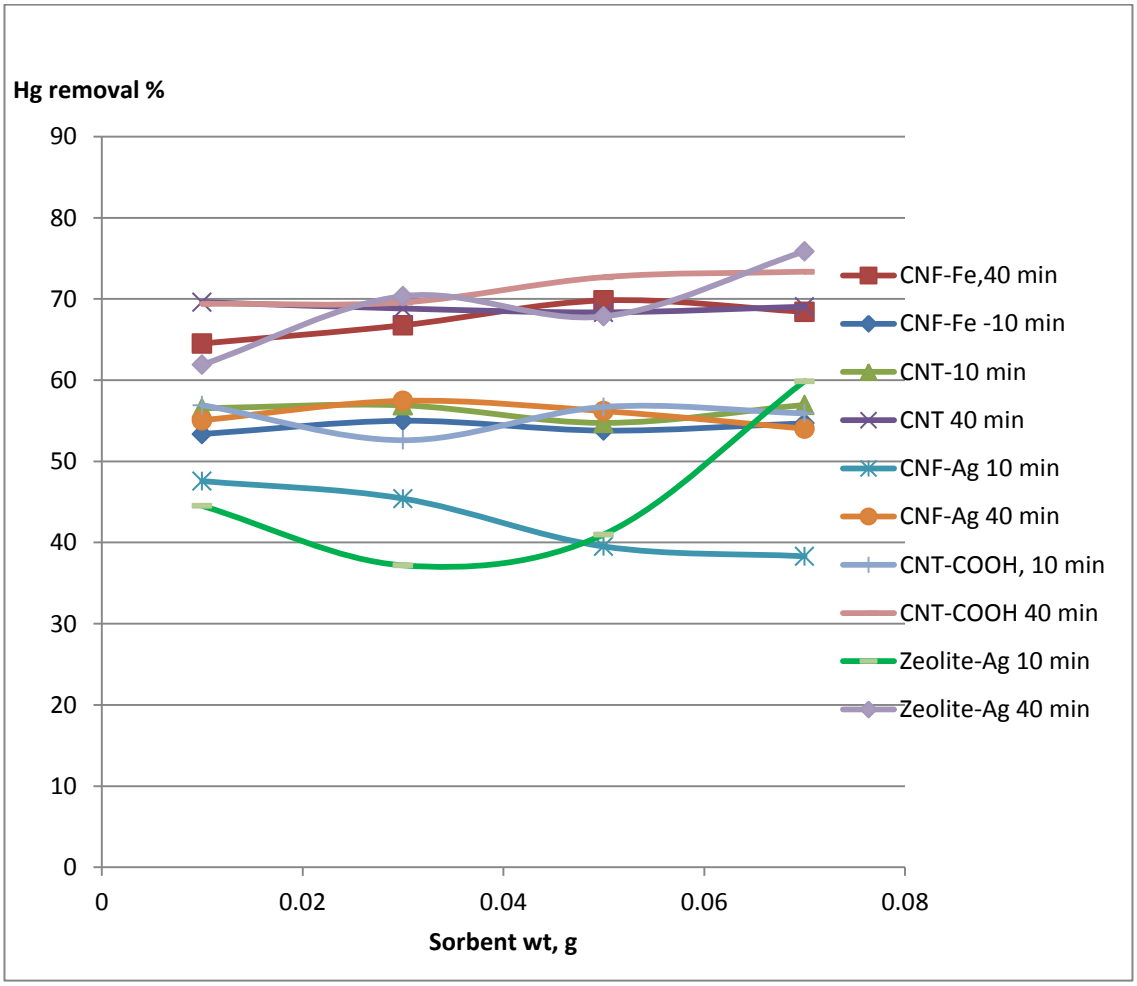


Figure 5.7. Mercury removal percentage of different sorbent doses at 10 and 40 minutes and fixed 200 rpm.

5.5 EFFECT OF SORBENT DOSES ON MERCURY REMOVAL AT DIFFERENT MIXING RATES AND FIXED CONTACT TIME

The effect of increasing sorbent weight at two different mixing rates 100 and 200 rpm and at fixed contact time of 40 minutes was evaluated. The overall results showed that the increase on the sorbent weight has minimal influence on the sorbent performance at fixed time and fixed mixing rate Figure 5.8. There is some improvement in mercury removal at a higher mixing rate. Overall, from this experiment and the previous ones, it can be concluded that the major factors that contribute to mercury removal efficiency are the mixing rate and contact time. The dosage has minimal impact on the mercury removal efficiency in the batch scale experiment.

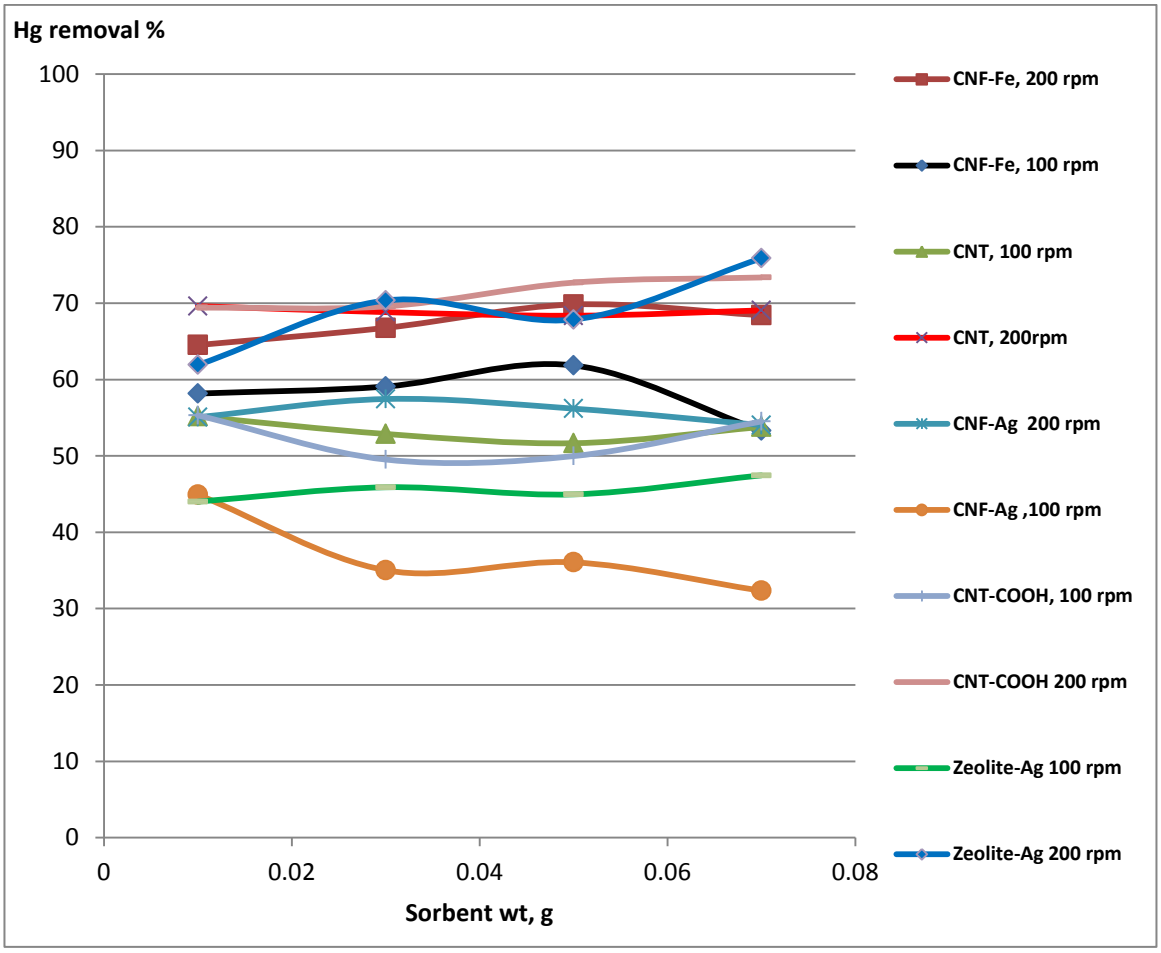


Figure 5.8. Mercury removal percentage of different dosages at 100 and 200 rpm and fixed time of 40 minutes.

The findings of this study will help evaluate the commercial sorbents using very simple lab batch setup. The sorbent performance can be ranked according to their ability of removing different mercury species under different condition such as contact time, mixing rate, and sorbent dosage. These factors will definitely help to make better assessment of selecting the appropriate sorbent for certain applications. Typically, the selection of the appropriate sorbent for industrial application is very challenging task and requires more experimental and pilot plant studies. Usually, the capacity and performance of a sorbent is evaluated using continuous flow of gas or liquid containing mercury over a bed of the sorbent for some time and monitoring the mercury content until it reach to the point where 100 percent break through achieved [84-86].

5.6 CONCLUSION

The study provided very fast and simple method to screen and evaluate the performance of commercial or new developed sorbents for mercury removal from liquid hydrocarbons using simple and fast lab screening methodology. The contact time and mixing rate were found to be the most critical factors that can help rank sorbents efficiencies. Using different mercury model compounds gave an additional important dimension to better assist the sorbent efficiency in removing mercury species. The data generated from this simple approach indicated that the comparison of various commercial or developed sorbents for actual field applications can be easily achieved. Sorbent doses which is also important, but not that significant on the lab scale experiment and can be replaced by the sorbent capacity (qe) which is an excellent indication of sorbent lifetime.

CHAPTER 6

SORBENTS PERFORMANCE USING MODEL COMPOUNDS

6.1 MERCURY MODEL COMPOUNDS

To evaluate the sorbents' performance of removing different species of mercury, four model compounds and some selected sorbents were used for this purpose. The model compounds used were mercury metal, mercury chloride, mercury alkyldithiocarbamate, and methylmercury chloride, to represent the various mercury species that may exist in the liquid hydrocarbon. Table 6.1 presents some of the physical properties of the gas condensate that was used to prepare the model compounds. Table 6.2 shows the mercury compound with their theoretical calculated mercury content and measured values concentration. The sample that was prepared using pure metal and $HgCl_2$ had very low solubility in gas condensate; where the measured soluble concentrations were always much lower than the expected calculated ones. This was not an issue for this study as the mercury content was always determined before and after each

experiments to avoid any measurement variations from mercury loss, by the deposition or sample evaporation, temperature variations, etc. Table 6.3 shows the solubility in water of different mercury species and Table 6.4 shows the solubility of mercury metal in different hydrocarbon solvents [87,88]. The same sorbents were studied for all prepared models compounds to consistently compare the effect of various mercury forms on the sorbents performance.

Table 6.1 Gas condensate properties

Gravity, °API	53.9
Sediment , Vol %	0.025
Sulfur, Total Weight %	0.04
Reid Vapor Pressure, psi	9
Hydrogen Sulfide, ppm	ND
Pour Point, (Upper),°F	-5
Salt, Lbs. NaCl/1000 BBL (PTB)	2
Ash, ppm	95
Microcarbon Residue, wt%	NIL
Nickel, ppm	<1
Nitrogen, ppm	4

Table 6.2 Mercury content in different model compounds

Mercury Species	Hg, ppb	
	Calculated	**Measured**
Methyl HgCl	222	226
Hg AlkylDithiocarbamate	201	207
Hg metal	66836	14323
$HgCl_2$	13712	730

Table 6.3 Solubility of different mercury species in water

Mercury Species	**Solubility, g/l**
Hg^0	5.6×10^{-5} at 25°C
$HgCl_2$	69 at 20°C
Hg_2Cl_2	2.0×10^{-3} at 25°C
CH_3HgCl	0.100 at 21°C
C_2H_6Hg	1 at 21°C

Table 6.4 Solubility of mercury in different solvents

Solvents	Solubility of Mercury, g/L
Water	5.62×10^{-4}
Isopropylether	9.63×10^{-3}
n-Hexane	1.26×10^{-2}
Cyclohexane	2.43×10^{-2}
Benzene	2.41×10^{-2}

6.2 REMOVING $HgCl_2$ USING DIFFERENT SORBENTS

The mercury removal percentage as Hg (II) from the model compounds using different sorbents ranged from about 6% to around 99.6% Figure 6.1. The commercial sorbent B gave the highest mercury removal performance. Some prepared sorbents did not show satisfactory performance removal of Hg (II). This is probably due to fact that Hg (II) has less reactivity to form any type of physical or chemical interactions with these sorbents where the commercial sorbents may have some material designed to make stronger physical or chemical binding to mercury (II).

The sulfur/carbon nanotube (SC) composite material designed by impregnating elemental sulfur into carbon nanotubes at different temperatures showed low mercury removal results. The mercury content in this model compound was considered to be 3-4 times higher than its content in a typical gas condensate. The carbon nanotube or carbon nanofibers have been widely used to remove heavy metals from aqueous media. The published work indicated that the ability of CNTs and CNFs of removing heavy metals depends mainly on their physical properties and not on the ions size of the heavy metals. In addition, the CNTs were found to have a strong tendency to adsorb organic compounds [88]. Therefore, the low efficiency of CNT and CNF and their modified forms may be attributed to the adsorption competition between organic compounds and mercury (II). The Zeolite and Alumina with impregnated silver also showed low efficiency

and this may be due to the low physical attraction between these material and Hg(II) Figure 6.1.

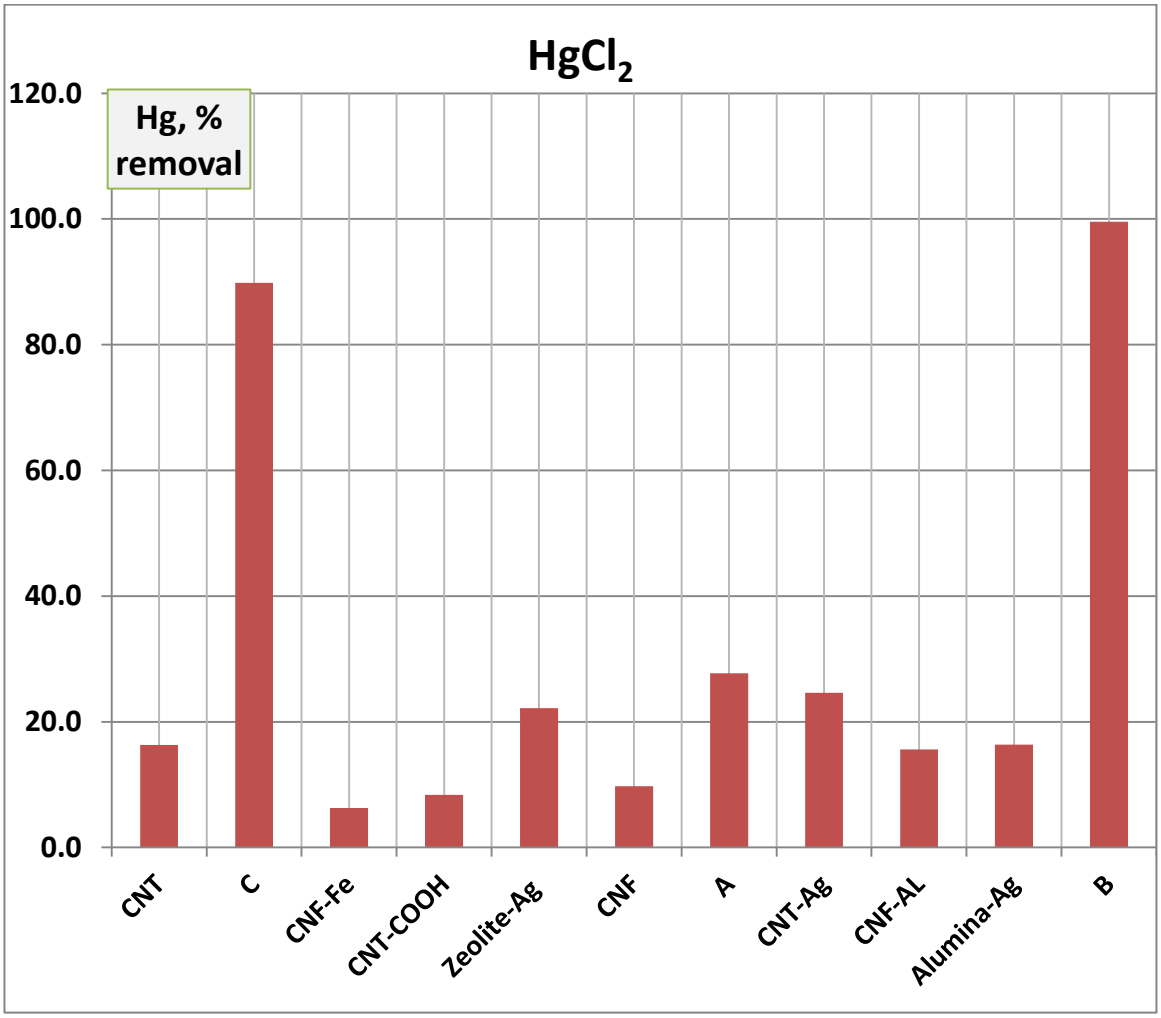


Figure 6.1. Various sorbents performance in removing Hg(II)

6.3 REMOVING METHYLMERCURY CHLORIDE USING DIFFERENT SORBENTS

All the sorbents did not perform well for removing Hg as methyl-Hg-Cl (MeHgCl) where the highest mercury recovery was around 45%, Figure 6.2. The MeHgCl seems to be very stable and thus lead to a low physical interaction with the sorbents material. Some of these sorbents performed better than others such as commercial material A, B and C. Also CNF-Fe, CNF-AL show a better ability of removing methyl mercury chloride than Hg(II).

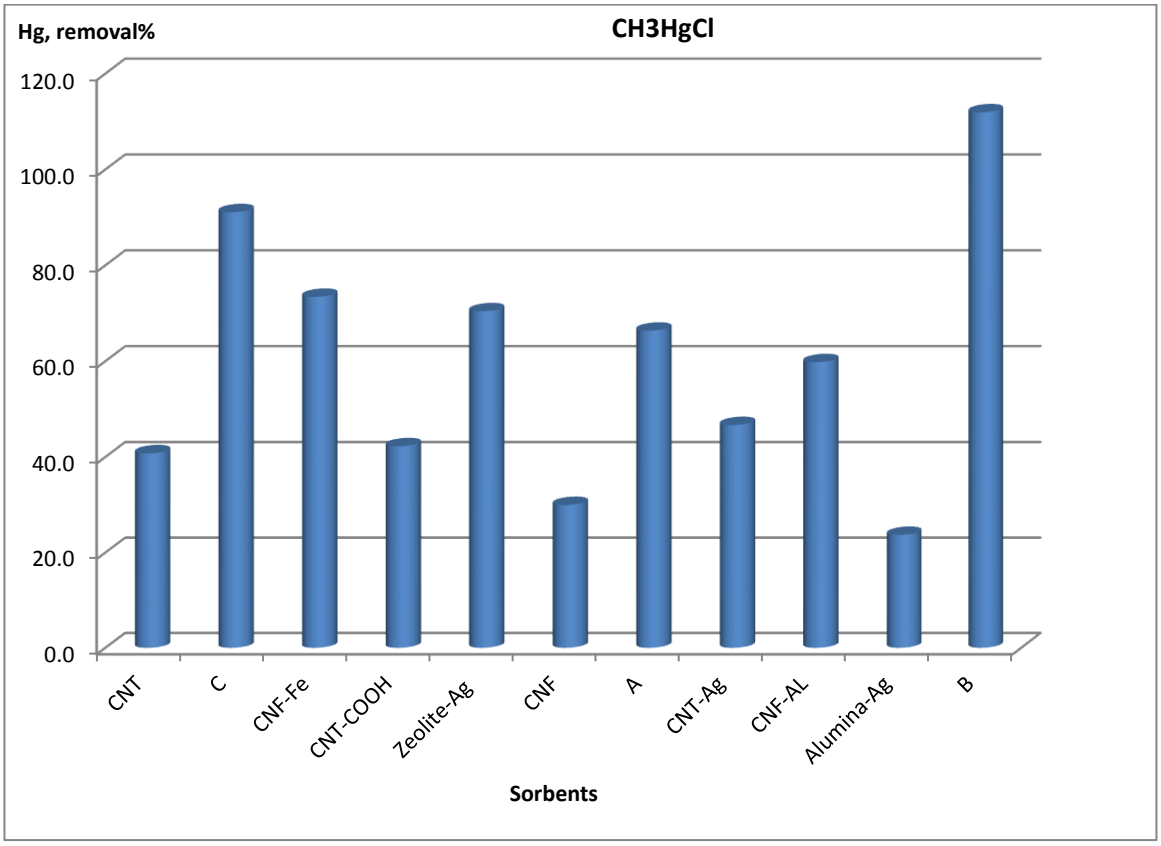


Figure 6.2. Various sorbents performance of removing CH_3HgCl

6.4 REMOVING MERCURY ALKYLDITHIOCARBAMATE USING DIFFERENT SORBENTS

Mercury alkyldithiocarbamate is used generally as a chemical standard for total mercury determination techniques due to its stability. This was used to represent some large mercury compounds that may exit in typical crude oil or gas condensate, such as biphenyl mercury. All the sorbents gave very low removal efficiencies below 30% except for sorbent C, which was around 75% mercury removal Figure 6.3.

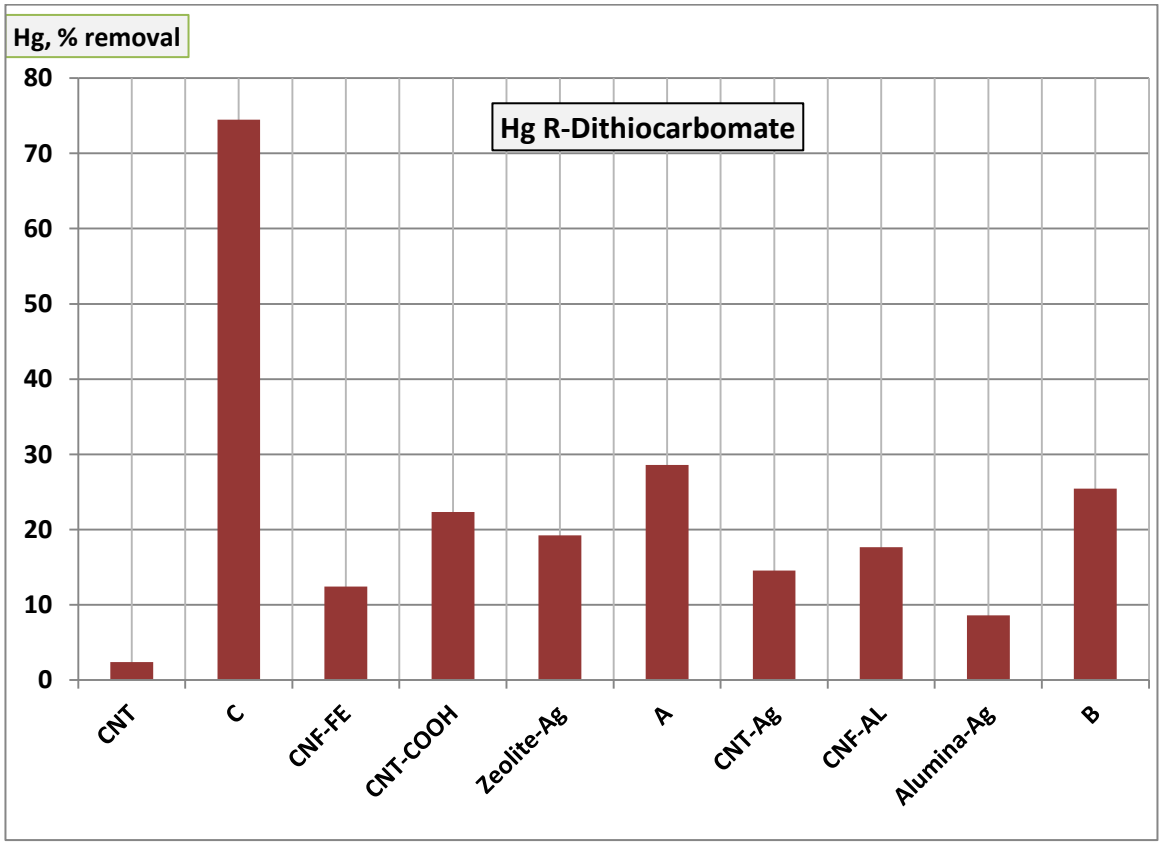


Figure 6.3. Various sorbents to remove Hg- alkyldithiocarbamate

6.5 REMOVING MERCURY METAL USING DIFFERENT SORBENTS

All sorbents performed well in removing mercury metal from gas condensate. Some gave high levels such as commercial sorbent C and CNT-Ag. In case of CNT-Ag, this is expected as it well known that Hg can form a strong amalgamation with Ag. Commercial sorbents were initially developed to address the removal of Hg metal from gas or light liquid hydrocarbons using some reactive components. The Hg removal percentage in Figure 6.4 did not reflect the actual performance of these sorbents due to the fact that the mercury content is already very high and the active components in these sorbents may vary from one to another. In addition, the surface area of these materials has a great influence on mercury removal.

To reflect the actual picture of the performance of these sorbents, the mercury concentrations, including both values removed and not removed were used to assist the sorbent performance, Figure 6.5. The mercury content in this model compound is considered to be too high compared with typical values that exist in gas condensate.

The mercury content measured in this experiment was found to be 3199 ppb. The model compound sample was not shaken for this experiment, to avoid getting high Hg concentration as most of the mercury metal precipitated. The mercury removed by these sorbents ranged from about 730-3050 ppb with the highest value demonstrated by the commercial

sorbent C. Therefore, all these sorbents will perform well with samples that include low levels of mercury metal content.

The efficiency of mercury removal sorbents will depend mainly on the type of Hg species exist in the sample as demonstrated by the model compounds experiments. Therefore, the mercury speciation in liquid hydrocarbon is critical for the development of the appropriate sorbents for mercury removal. Figures 6.4 and 6.5 are two examples that demonstrate this fact. In Figure 6.4 the carbon nanotube modified with iron gave mercury removal efficiency in the following order MeHgCl> Hg metal > Hg alkyldithiocarbamate > $HgCl_2$.

The commercial sorbent A and the prepared carbon nanotube impregnated with silver show close results of removing mercury in the form of MeHgCl, and Hg alkyldithiocarbamate with a slight advantage shown by sorbent A. Sorbent A gave almost twice the efficiency of CNT-Ag of removing mercury in the form of $HgCl_2$, and CNT-Ag gave almost three times the efficiency of sorbent A in removing mercury metal.

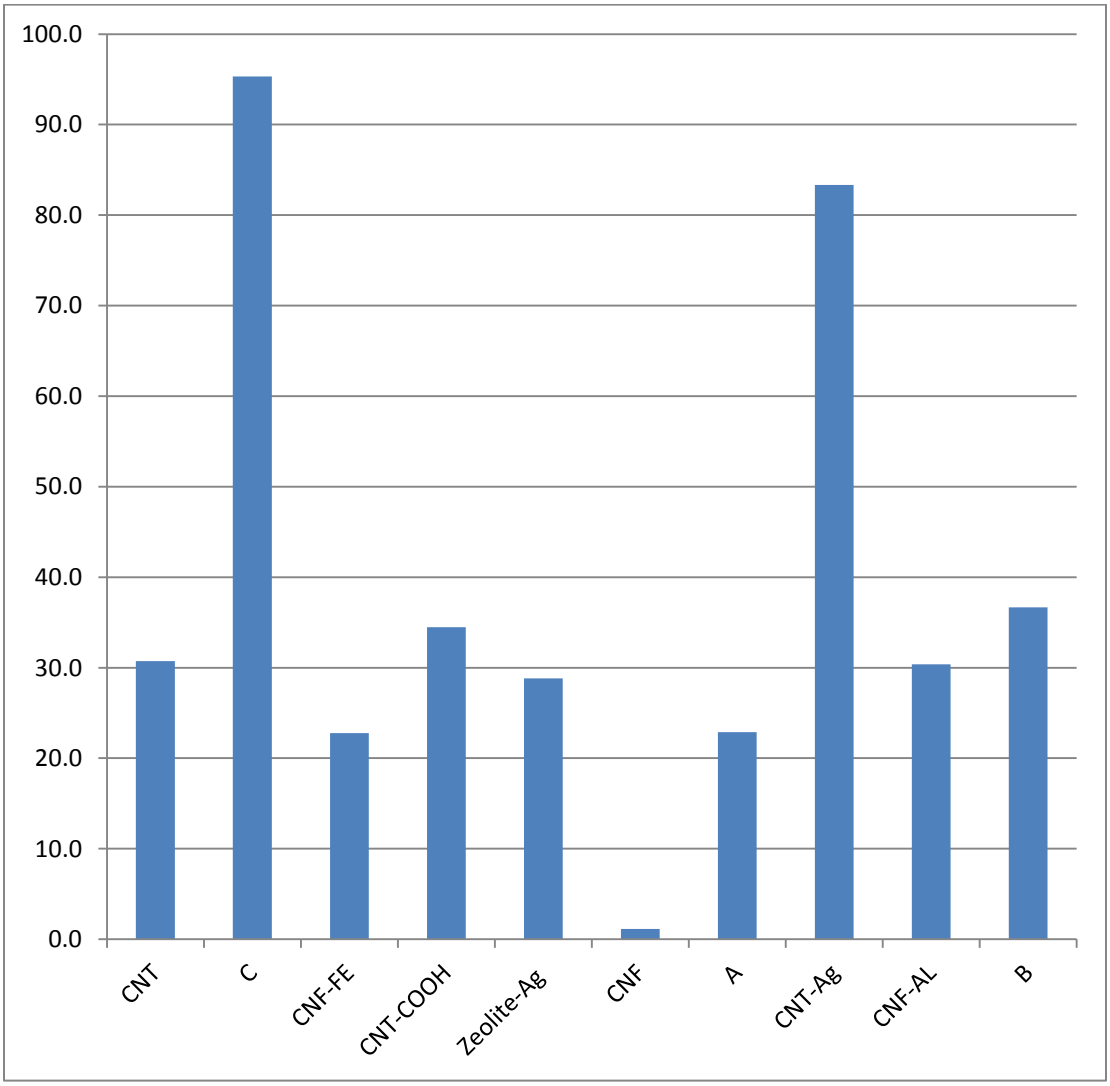


Figure 6.4. Various sorbents to remove Hg metal

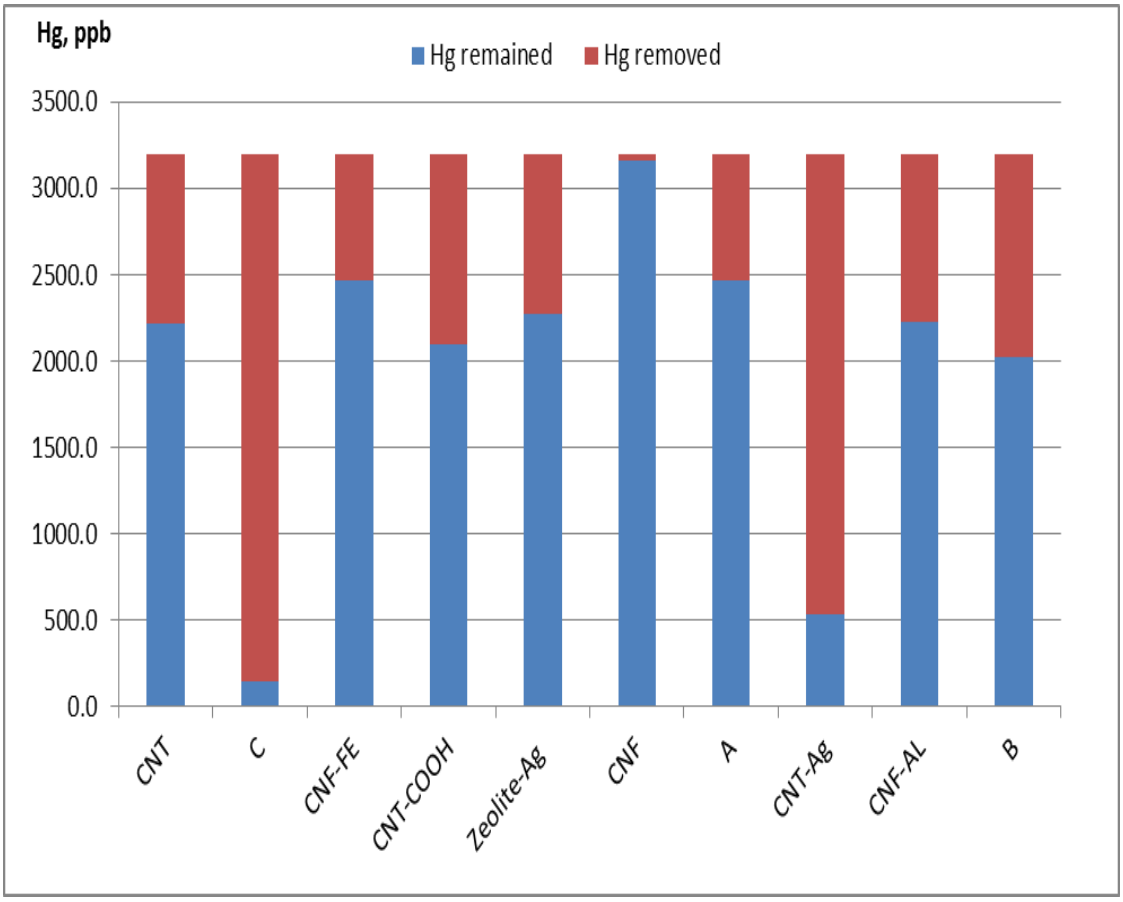


Figure 6.5. Removed and remaining Hg metal content using various sorbents

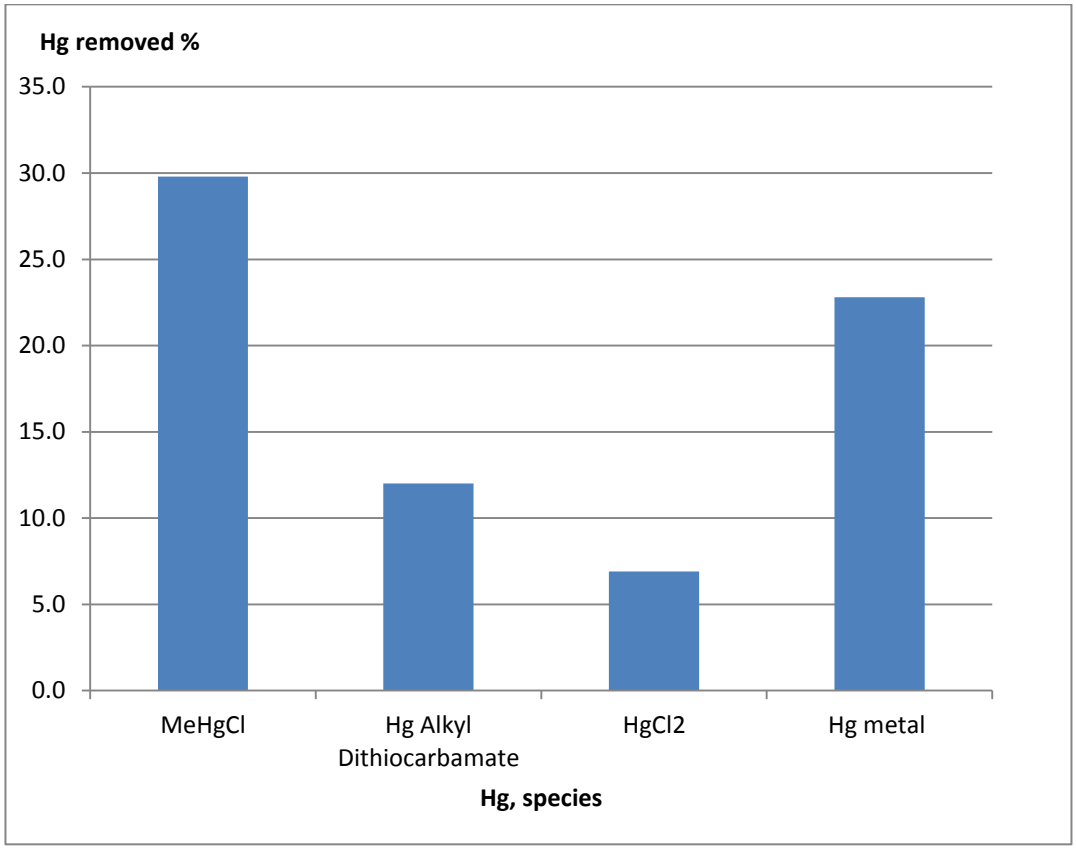


Figure 6.6. Hg percentage removal from different Hg species model compounds using carbon nanotubes impregnated with Fe

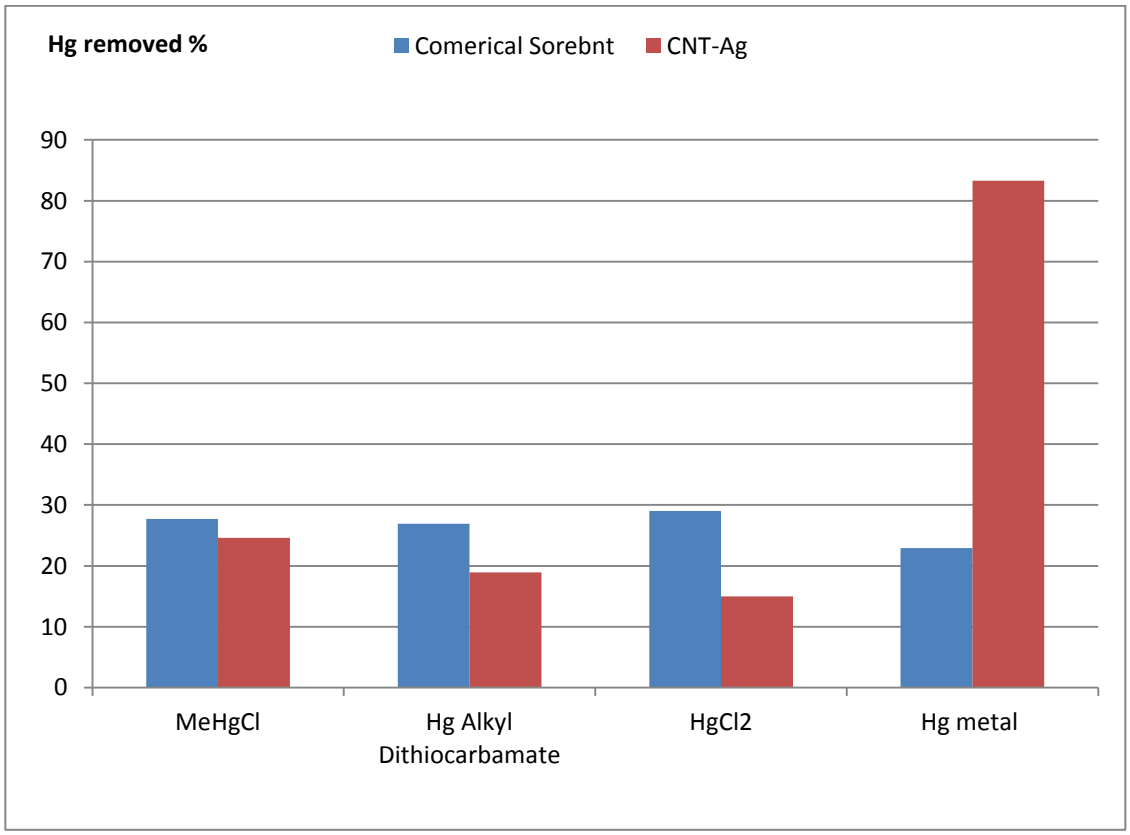


Figure 6.7. Comparison of Hg percentage removal of different Hg species in model compounds using carbon nanotube silver and commercial sorbent A

6.6 CONCLUSION

The sorbents performance of removing mercury from liquid hydrocarbons can be evaluated using the different forms of mercury. The study showed that some sorbents are very effective in removing mercury metal and mercury (II) while others showed low performance in removing other organic mercury compounds. The mercury speciation in liquid hydrocarbon seems to be very challenging task due to several factors such as the gas condensate chemical and physical properties and compositions, the possibility of mercury lost, the chemical and physical interaction between mercury and hydrocarbons or interconversion process that may take place. Therefore, the use of mercury model containing different forms of mercury will be of a great help during the sorbents development and performance evaluation.

CHAPTER 7

EVALUATION OF SORBENTS PERFORMANCE

Various sorbents material was prepared in addition to some available material, Table 7.1. These sorbents were tested for their ability of removing mercury from actual gas condensate and from prepared model compounds that contains different mercury forms. Gas condensate samples were collected as needed for all experiments, to avoid losing some of the mercury content or types, as seen in the mercury speciation study. All parameters and conditions were fixed, e.g., gas condensate sample source and volume, shaking time, mixing rate, and the sorbents weights — except for carbon nanofibers series where different weights were taken due to the low density of these materials.

Table 7.1 Various Sorbent Types used

Sorbents Types	
Activated Carbon (AC) Series	**Flay Ash series (FA)**
AC	FA
AC-Cu	FA-COOH
AC-Fe	FA-Cu
AC-Al	FA-Al
AC-Ti	FA-Ti
AC-Ag	FA-Ag
AC-COOH	FA-Fe
Carbon nanotubes (CNF) series	**Carbon nanotubes (CNT) series**
CNF	CNT-Ti
CNF-Ag	CNT
CNF-Al	CNT-Ag
CNF-Cu	CNT-Cu
CNF-Fe	CNT-Al
CNF-COOH	CNT-COOH
	CNT-Fe
Alumina series	**Zeolite series**
Alumina	Zeolite
Alumina +KI	Zeolite+Ki
Alumina+ Ag	Zeolite+Ag
Commercial Sorbents	
A	
B	
C	

7.1 FLY ASH (FA) AND ITS MODIFIED FORMS

Fly ash and its modified forms using Fe, Ti, Al, Cu, Ag carboxylic and hydroxyl groups showed good performance of removing mercury from gas condensate Figure 7.1. These modified sorbents were ranked according to their performance of removing mercury, indicating that the fly ash impregnated with iron gave higher mercury removal percentage where fly ash without functionalization gave the lowest removal percentage. The fly ash material used in this experiment is the product from burning crude or fuel oil in some of the local power plants. Typical material is composed of different components such as silica, alumina, iron oxide, and calcium, with varying amounts of carbon, depending on the type and source of crude or fuel oil used as fuel in the power plants [89]. Figure 7.2 and 7.3 shows the ESEM and EDS showing the major elements that exist in flay ash material used in this study

Historically, this material has been used in different applications such as: an adsorbent for mercury removal from gas flues, or blending the fly ash with other material such as concrete or asphalt [89].

Although the fly ash includes some metals, they are not reactive to make strong interaction with mercury species in the liquid hydrocarbons. This could be attributed to the formation of stable metal compounds with low tendencies to form any complexation with mercury species. The results show that the

performance of different modified fly ash forms increased in the following order FA>FA-COOH>Fe-Cu>FA-Al>FA-Ti>FA-Ag>FA-Fe. Since the media used is liquid hydrocarbon, there will be always competition by other hydrocarbon components that may have higher adsorbent affinity to fly ash surface than mercury species, and thus may reduce the performance of fly ash in removing mercury. The advantages of using fly ash as a sorbent for mercury removal in liquid hydrocarbon include: the availability of such material with no cost, as it is a waste product with high service area and easily modified with other material. The low density and fine powder particles are disadvantageous for use in liquid hydrocarbon where the particles tend to dissolve and stay in the hydrocarbon phase, which may require a special design to handle and remove it from the liquid hydrocarbon streams.

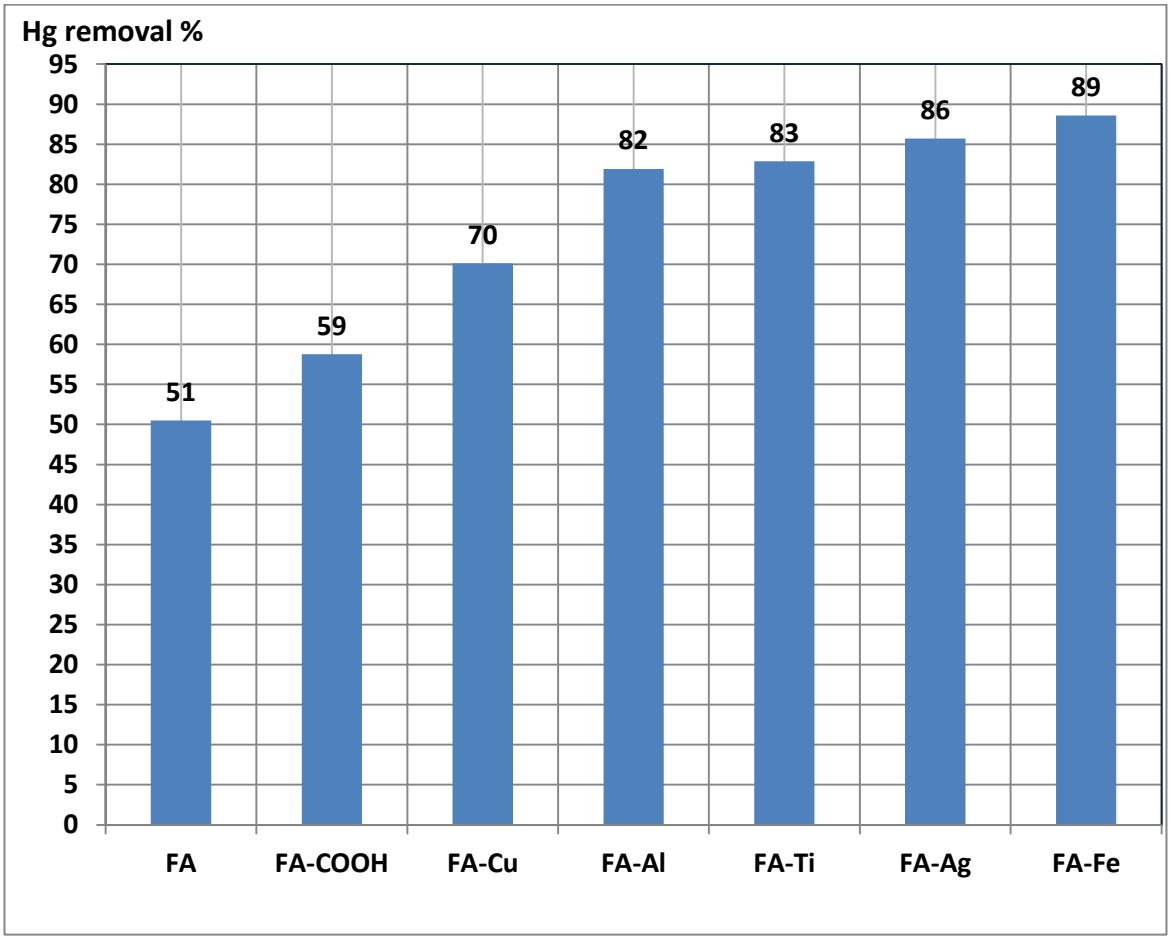


Figure 7.1. Hg removal% with different fly ash and its modified forms.

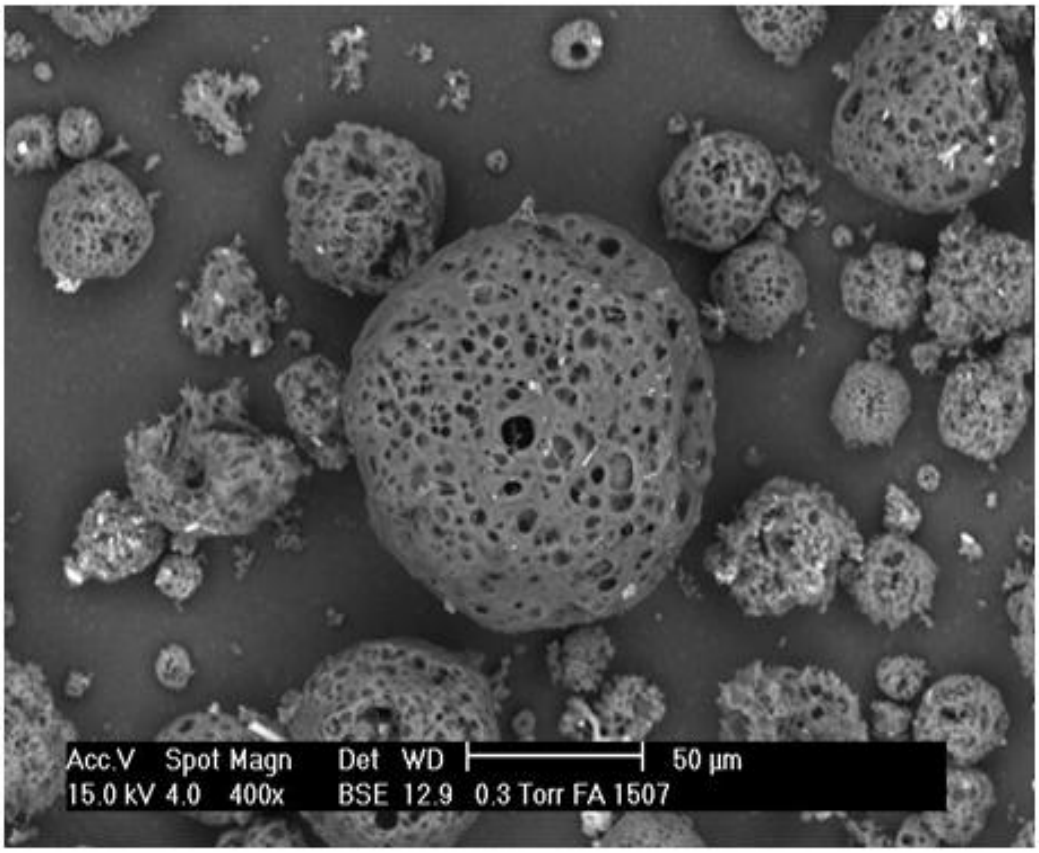


Figure 7.2. ESEM of fly ash

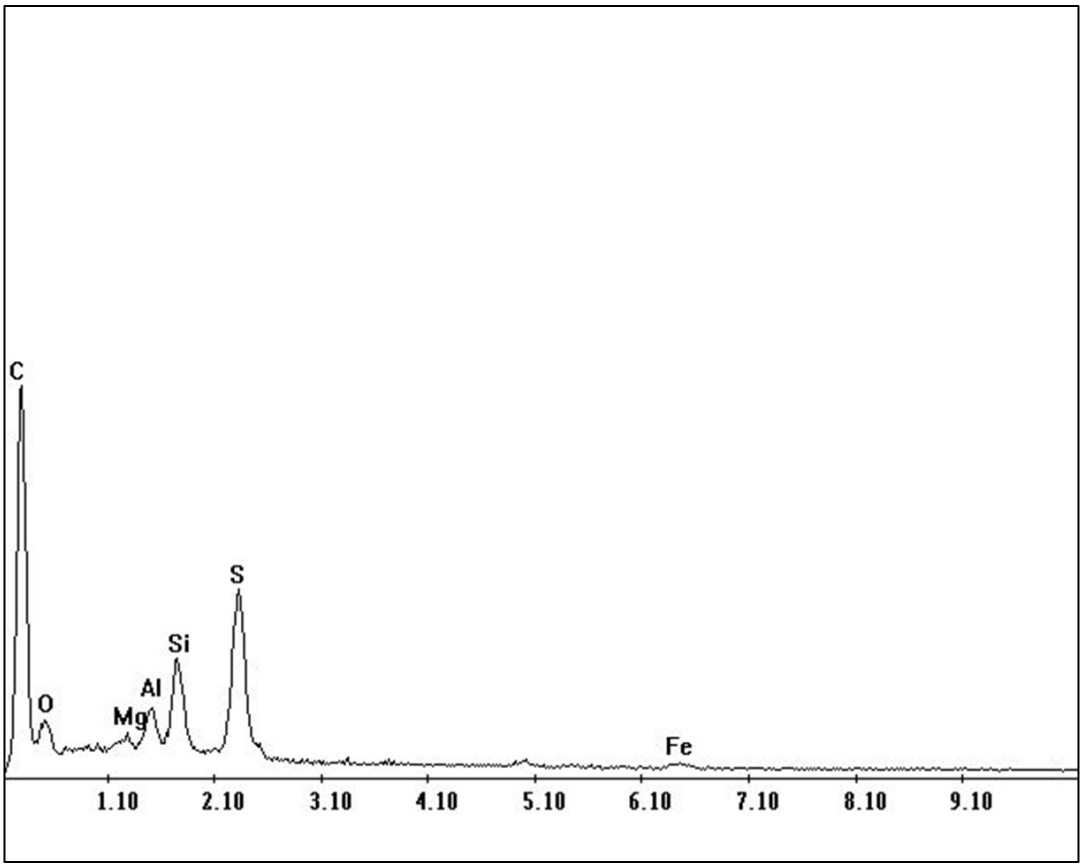


Figure 7.3**.** EDX of fly ash

7.2 CARBON NANOTUBE (CNTs) AND ITS MODIFIED FORMS

The CNT and its functionalized forms provided excellent mercury removal ranging from 50 to 92%. CNT without any functionalizing was able to remove mercury by as much as 73%, Figure 7.4. The efficiency of removing mercury from liquid hydrocarbon increased in this order: CNT-Ti→CNT≈CNT-Ag→CNT-CU→CNT-Al→CNT-COOH→CNT-Fe. Previous work conducted on removing mercury (II) from aqueous solution using CNT indicated that there is high affinity between the CNT surface and Hg (II). This is probably applicable to mercury in the liquid hydrocarbon; however the CNT has also strong affinity to hydrocarbon compounds [57, 94]. This will create some competition between mercury and other hydrocarbon compounds to make strong adsorption with CNT or its modified forms surface. The CNTs modified with Fe (III) show high efficiency in removing mercury from actual gas condensate. CNTs functionalized with COOH group show excellent mercury removal efficiency indicating that in addition to the adsorption phenomena, there is complexation process taking place between COOH group and mercury species.

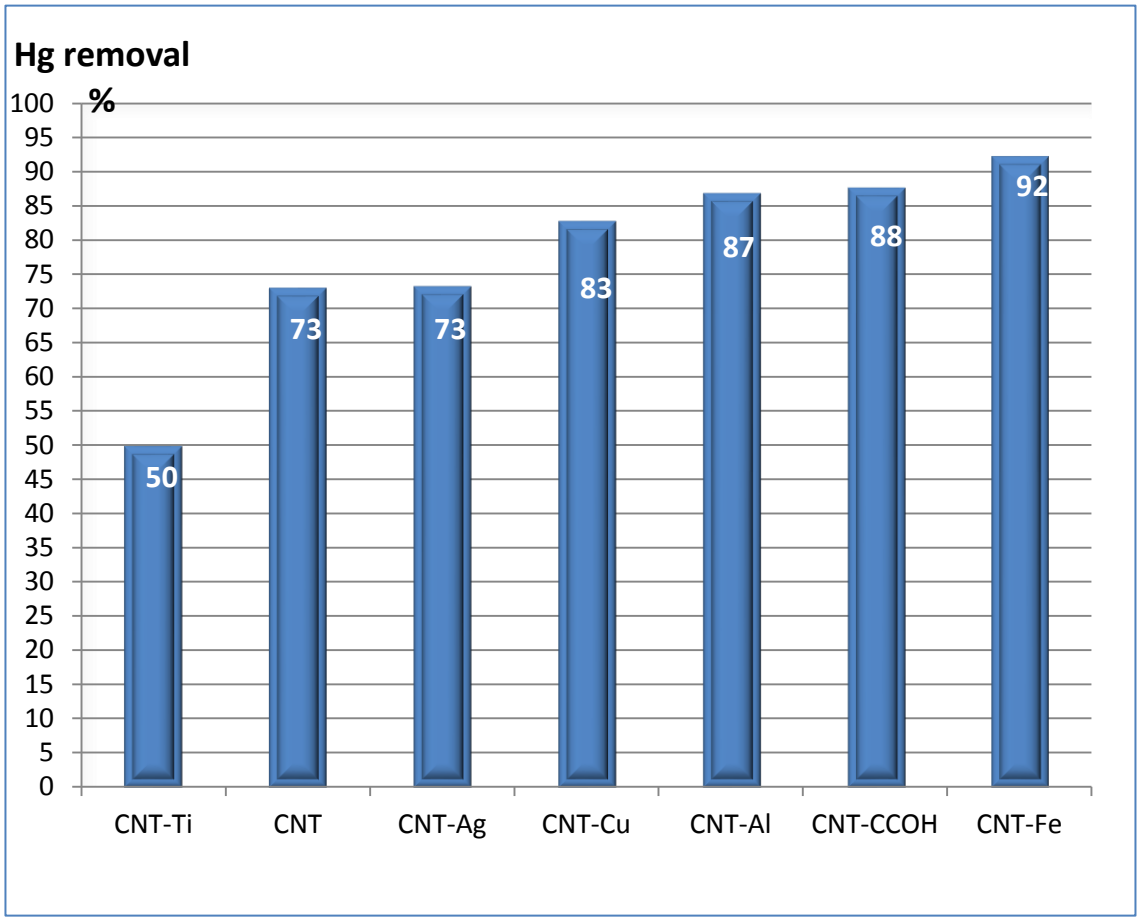


Figure 7.4. Hg removal % using CNT and its different modified forms

7.3 CARBON NANOFIBER (CNF) AND ITS MODIFIED FORMS

Carbon nanofiber series has demonstrated good performance in removing mercury from gas condensate, Figure 7.5. Due to the low density of some of the CNFs series, less and varied weights were taken for this experiment and therefore the mercury removal percentage is not a good indication to compare the performance of this series.

The adsorption capacity in Figure 7.6 shows that the CNF-Fe has the highest mercury capacity to remove mercury followed by CNF. The graph in Figure 7.7 compares the mercury removal performance of both series of CNT and CNF using the adsorption capacity equation. The findings indicate that the CNF series resulted in a better performance than the CNT series. The larger diameters of CNF provide high service area, which consequently could influence the mercury removal performance. Generally, the difference between the carbon nanotubes and carbon nanofibers is related to their chemical structure. The CNT is made from graphene layers that rolled in a cylindrical shape with a plane parallel to the fiber axis, with typical tube diameter ranging from 10-50 nm. The CNF is made of graphene that rolled up in a form perpendicular to the fiber axis with a larger diameter ranging from 50-200 nanometers [90]. The Figure 7.8 shows an example of CNT-Fe and CNF-Fe ESEM images for comparison.

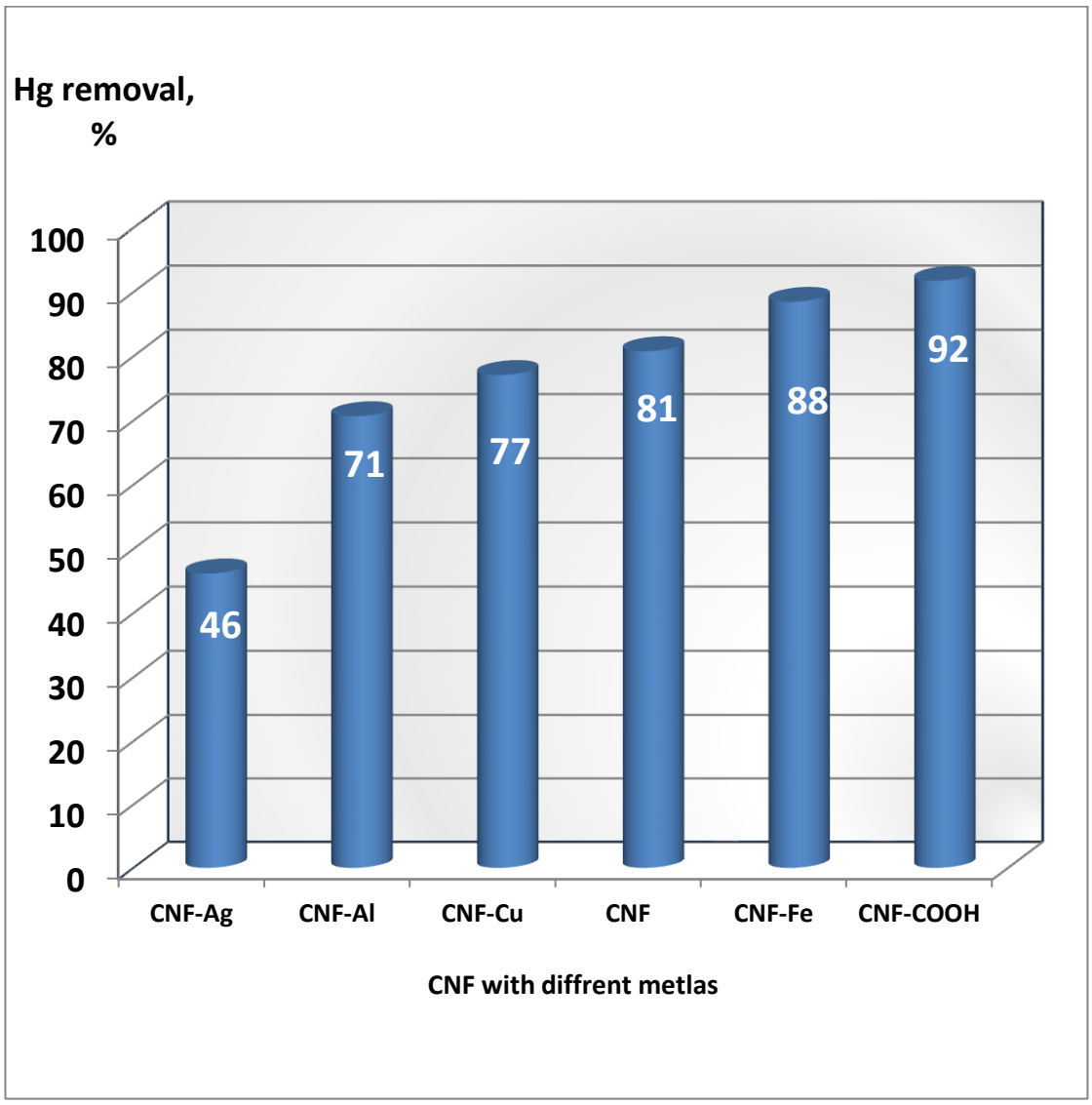


Figure 7.5. Mercury removal percentage using CNF and its modified forms

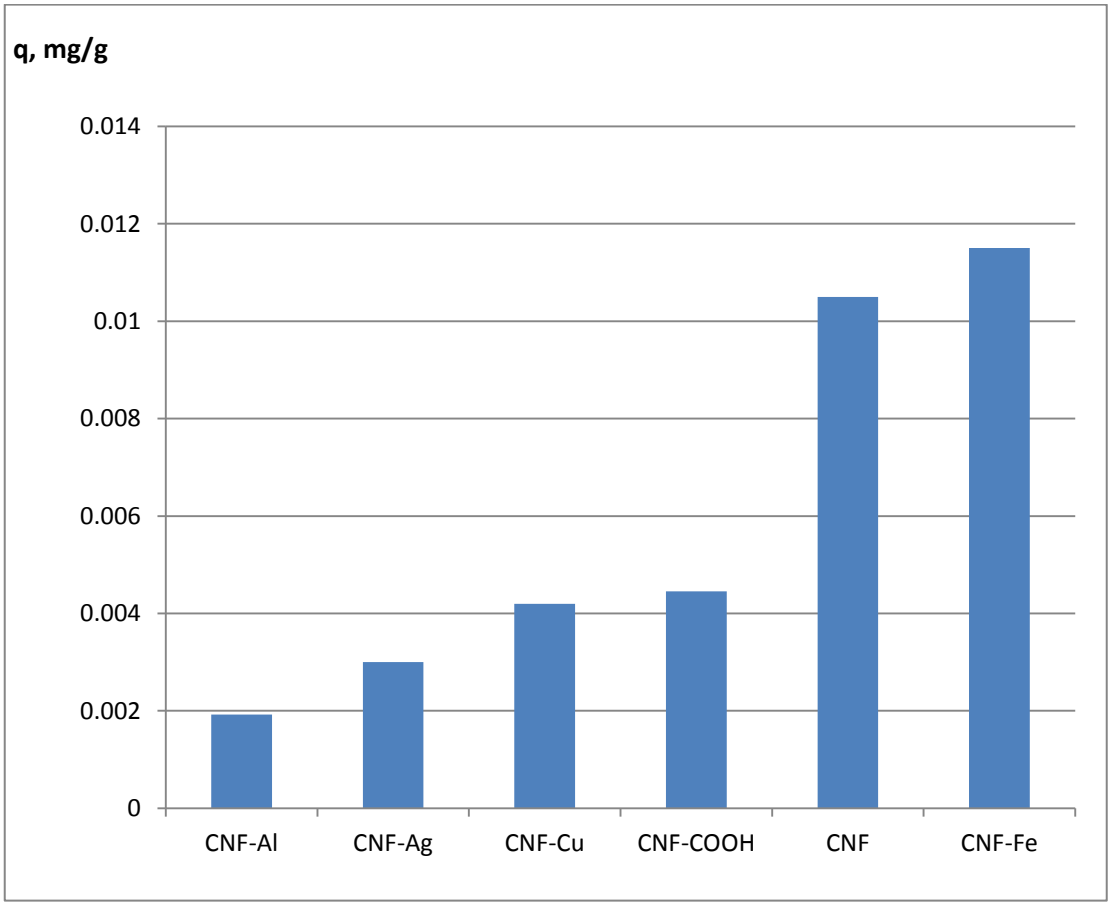


Figure 7.6. The adsorption capacity of CNFs and its modified forms

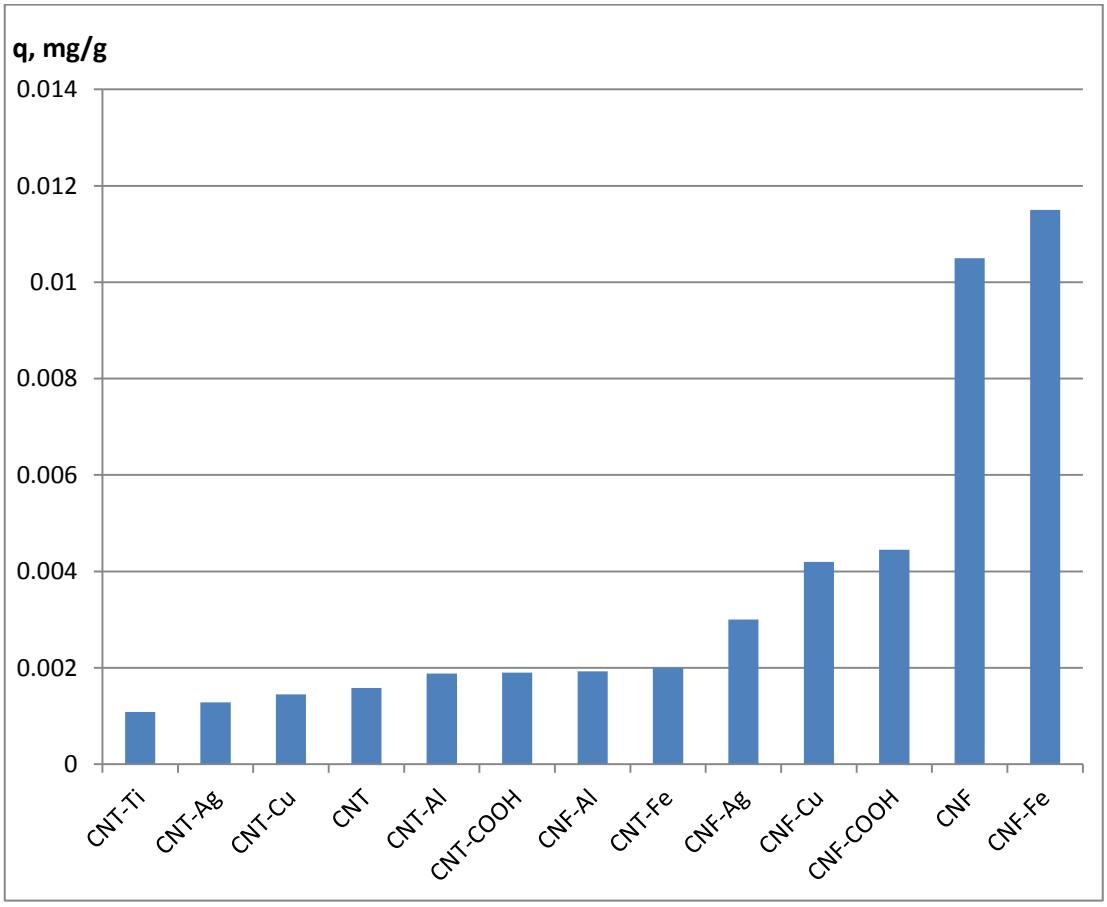


Figure 7.7. The adsorption capacity of CNFs and CNTs and their modified forms

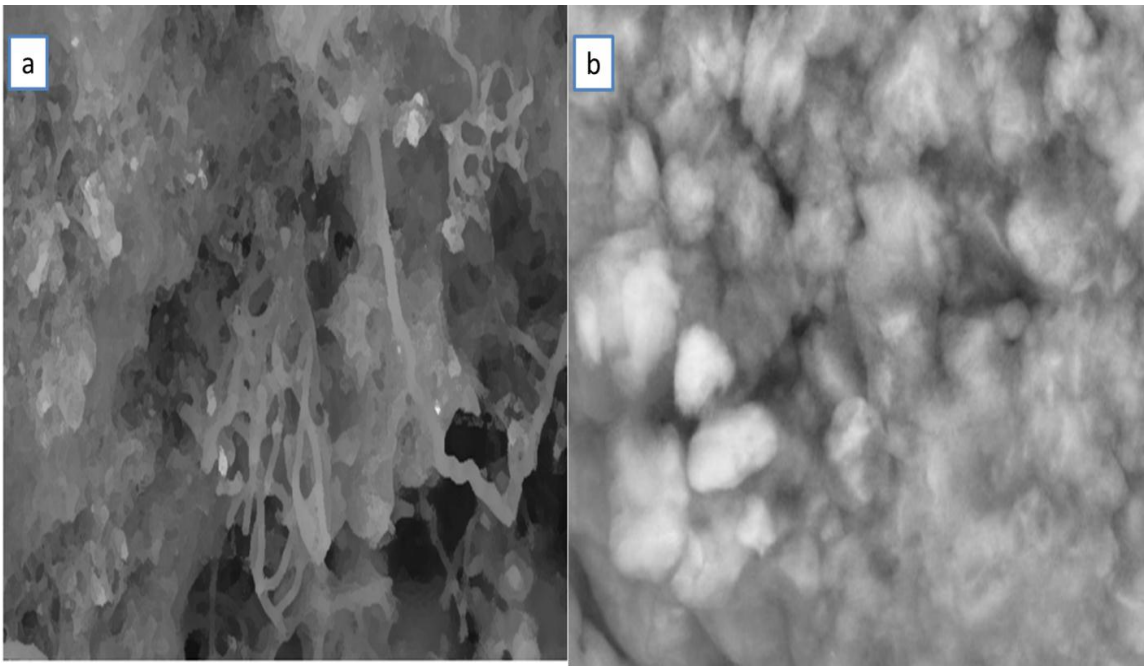


Figure 7.8. ESM images (a) CNF-Fe (b) CNT-Fe at 2500x

7.4 ACTIVATED CARBON (AC) AND ITS MODIFIED FORMS

The activated carbon impregnated with Cu, Fe, Ag, Al, Ti ions were evaluated for removing mercury from gas condensate. The results in Figure 7.9 show that all AC with different metals performed well and gave close results, except for the copper ion, which may be related to the interaction between the Cu and the AC material or with mercury species. Activated carbon alone or impregnated with other elements such as potassium iodide or sulfur-metal are commonly used to remove mercury from petroleum or coal fired power plant gas emission, or from natural gas processing, medical incinerators, etc.[91-95].

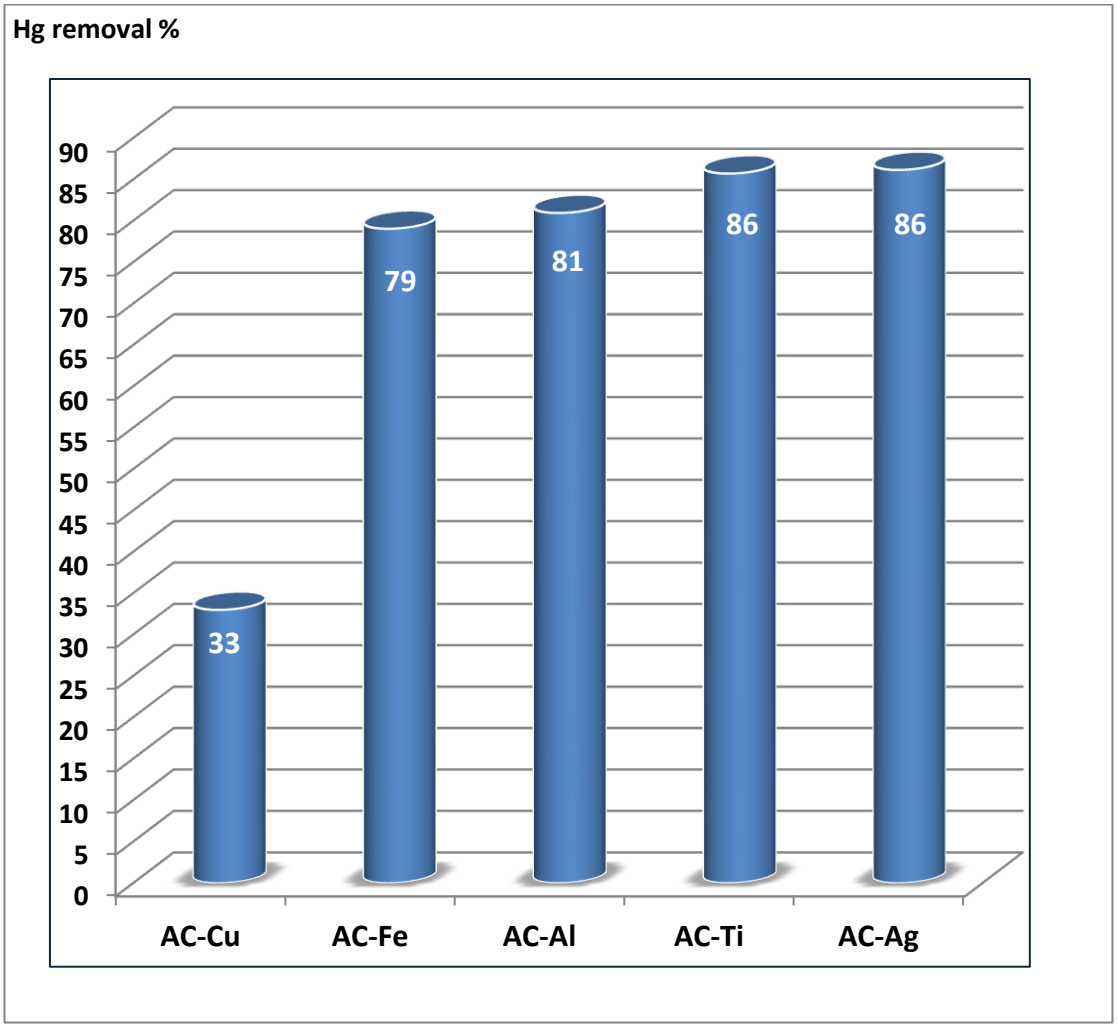


Figure 7.9. Hg removal% using AC and its modified forms

7.5 ALUMINA AND ITS MODIFIED FORMS

Alumina alone or impregnated with KI and Ag gave good performance of mercury removal Figure 7.10. The alumina without any modification performed better than the ones impregnated with KI and Ag, indicating that the alumina surface has better active sites to adsorb mercury species in gas condensate. The gas condensate sample as demonstrated by the mercury speciation study chapter 4, seems to have mostly mercury metal and organic Hg species. The silver is well known to make strong amalgamation with mercury; however it has less interaction with organic species, as was observed on the model compounds study. The alumina seems to have a strong physical adsorption of Hg organic species in addition to the mercury metal. The other reason that alumina impregnated with KI and Ag may make strong chemical and physical adsorption with Hg species, however the formed complexes might undergo a desorption process. These Hg complexes leave the support material and stay in the liquid hydrocarbon phase where they are included in the total mercury measurements.

Alumina is basically Al_2O_3 where it used in many industrial applications. It is worth mentioning that the Al_2O_3 is a product formed by reacting mercury with aluminum of the heat exchangers tubes at the natural gas processing plants. In fact the reason for developing mercury sorbent material is to protect these heat exchangers [2]. Aluminum amalgamates first with mercury and then reacts in the presence of moister under oxidation reduction process releasing the mercury

metal again to the stream. This process causes loss of the heat and eventually damages the tubes. The reaction is described below [1]

$Hg + Al \rightarrow$ Hg-Al amalgam

$2Hg\text{-}Al + 6H_2O \rightarrow Al_2O_3.3H_2O + 3H_2 + 2Hg$

Therefore, according to the above reaction the mercury keeps regenerating and continues its reaction cycle. It will also transfer during this process with the flow stream and eventually will end up in the product.

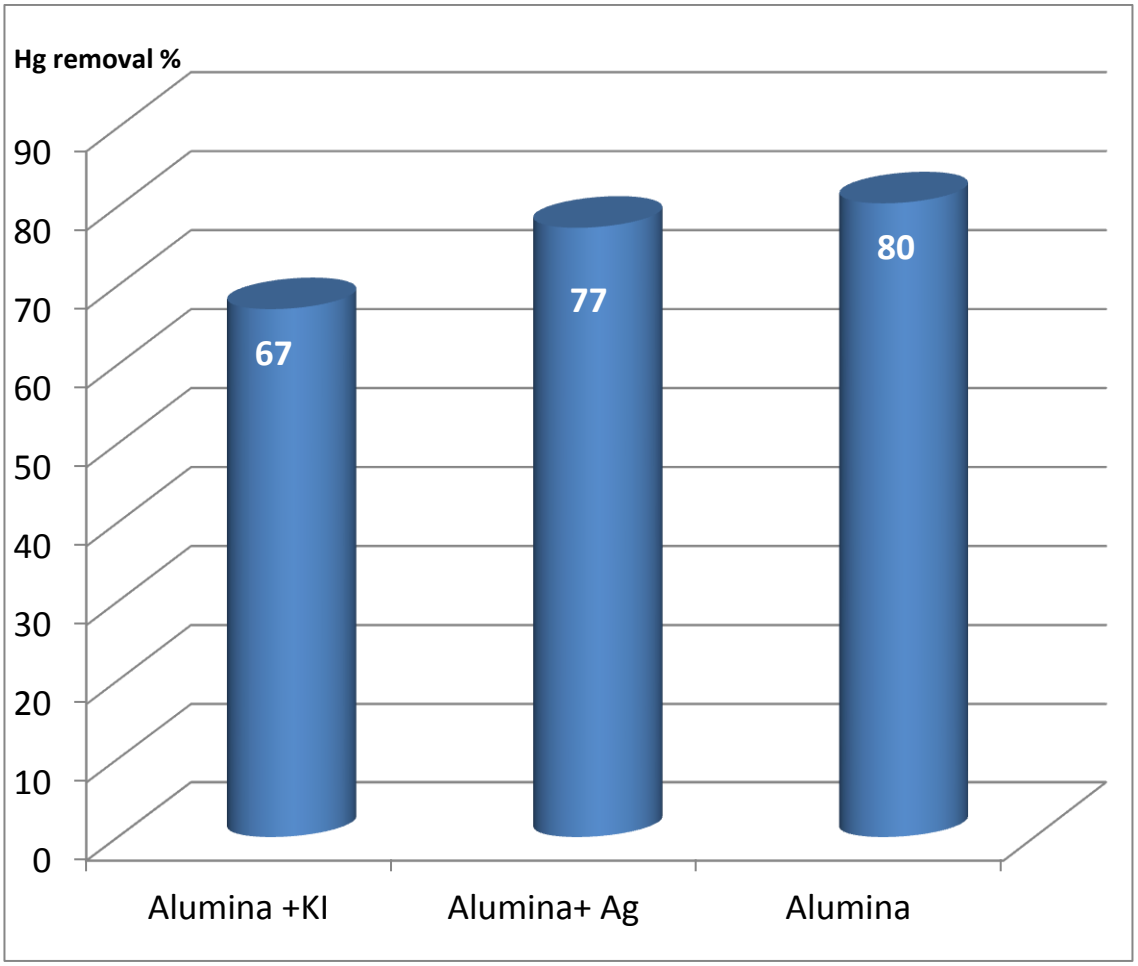


Figure 7.10. Hg removal % using Alumina and its modified forms

7.6 ZEOLITE AND ITS MODIFIED FORMS

Zeolite impregnated with silver ion performed much better than the neat zeolite or impregnated with KI, Figure 7.11. Zeolite is basically mixture of silica and alumina (SiO_2/Al_2O_3) prepared at different ratios according to their applications. Zeolite series did not perform well compared to alumina series. The mercury removal efficiency seems to be mainly affected by the alumina part of the zeolite. This can be seen in Figure 7.12, which compared the mercury removal efficiency of the two sorbents series. The alumina gave around 88% mercury removal where the zeolite provided only about 66%. The alumina and zeolite impregnated with silver have very close mercury removal efficiency and gave mercury close to 80% mercury removal. The alumina and zeolite impregnated with KI gave around 67% and 58% mercury removal respectively. In general alumina and zeolites seems to provide good mercury removal and therefore they should be tried at larger scale to evaluate their actual performance.

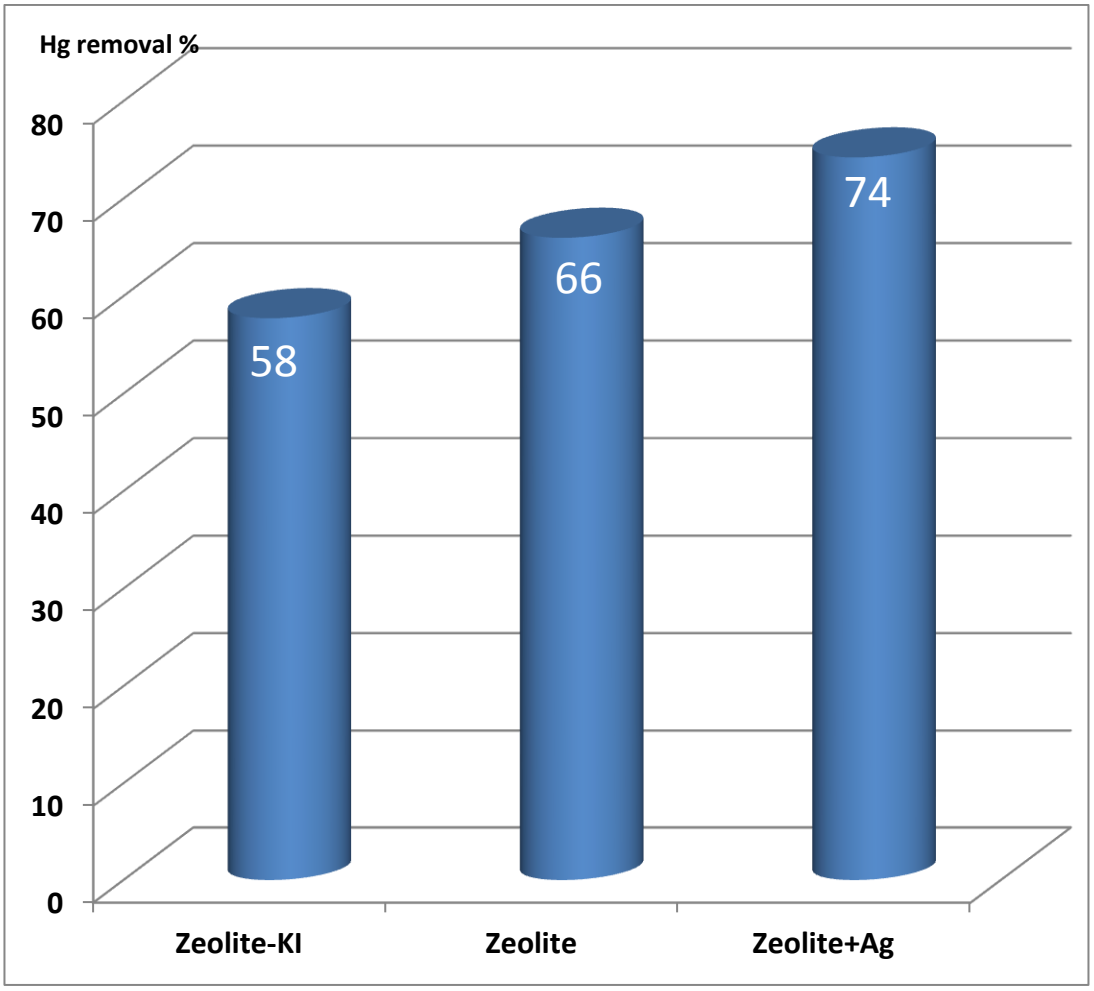


Figure 7.11. Hg removal % using zeolite and its modified forms

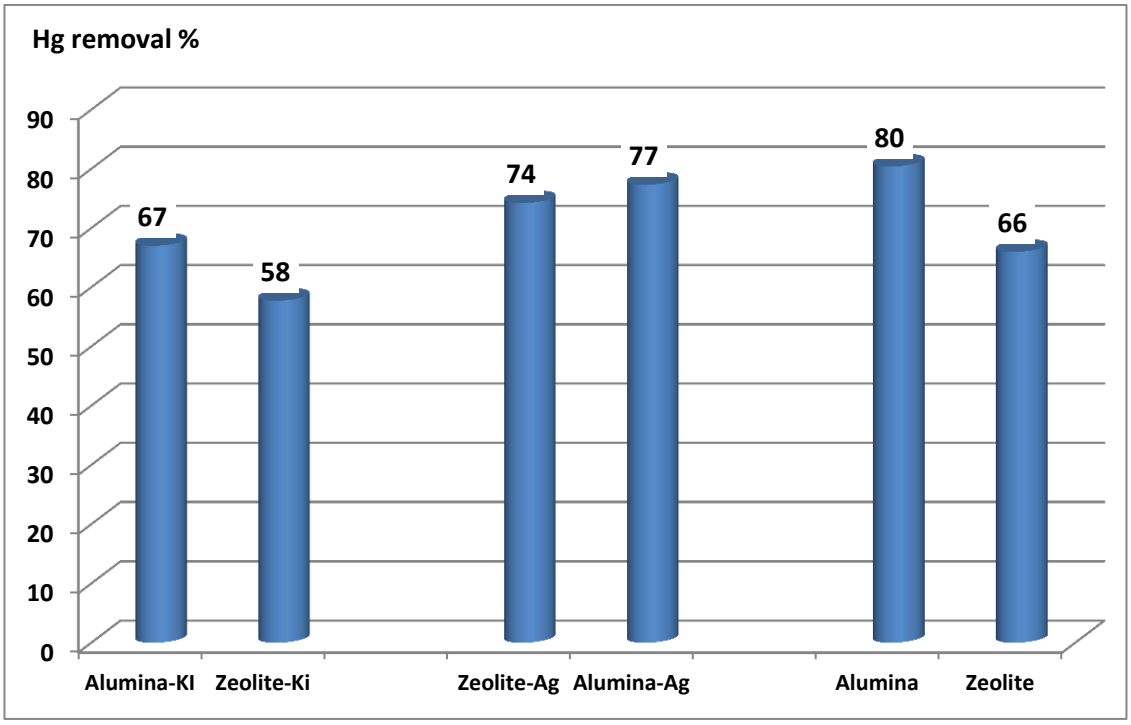


Figure 7.12 Comparison of Hg removal % of Zeolite and Alumina and their modified forms.

7.7 CONCLUSION

Several novel sorbents were developed utilizing carbon nanotubes and nanofibers (CNTs, CNFs), activated carbon, (AC) flay ash (FA), alumina, zeolite and their modified forms by certain active components. These sorbents were tested for mercury removal from gas condensate and some prepared model compounds. The results indicate that most of the prepared sorbents showed very good performance in removing mercury from gas condensate where sorbents modified by iron showed the highest mercury removal. The mercury species play a key role in the sorbents performance, where mercury metal in the model compound was removed more easily than other mercury species. Some of the prepared sorbents performance exceeded the ones of commercial sorbents.

7.8 FUTURE WORK

The sorbents will be scaled up for field applications to remove mercury from whole gas condensate at the upstream production conditions. This new innovative approach may lead to successful technologies that capable of removing mercury from the upstream and thus avoid all issues related to mercury at the downstream operation.

CHAPTER 8

REMOVING MERCURY USING ELEMENTAL SULFUR IMPREGNATED ON CARBON NANOTUBES

8.1 EVALUATION OF SORBENT PERFORMANCE

New materials based on impregnating elemental sulfur on multiwall carbon nanotubes, were prepared at different temperatures, and tested for their ability to remove mercury from gas condensate and mercury model compounds. This approach was based on the utilization of sulfur affinity toward mercury species particularly the elemental mercury. The conventional way of impregnating sulfur physically on the support material has some limitations. Sulfur can be easily dissolved in liquid hydrocarbon, leading to becoming a major contamination of the hydrocarbon streams and creating problems in the downstream process. The sulfur reacts with mercury species forming different complexes that can be desorbed from the support material and transferred to the liquid hydrocarbon streams, resulting in poor sorbent mercury efficiency removal. Therefore, this

study explored the possibility of reacting elemental sulfur with carbon nanotubes chemically to form a stable sulfur–mercury complex. Table 8.1 shows a list of materials prepared at different temperatures, which were tested first to see their ability to remove mercury from actual gas condensate, Figure 8.1. The mercury removal percentage ranged from about 11% to around 64%. The adsorbent capacity (qe) was used to compare their performances since different weights were used, Figure 8.2. The sulfur impregnated carbon nanotubes prepared at 500 °C gave the highest mercury removal, followed by the one prepared at 400 ºC.

Table 8.1. The sulfur/carbon nanotubes (SC) prepared at different temperatures

Sulfur Carbon Nanotubes	**Temperature Used**
SC100	100 °C
SC200	200 °C
SC 300	300 °C
SC400	400 °C
SC500	500 °C
SC900	900 °C
SC1000	1000 °C
SC1100	1100 °C

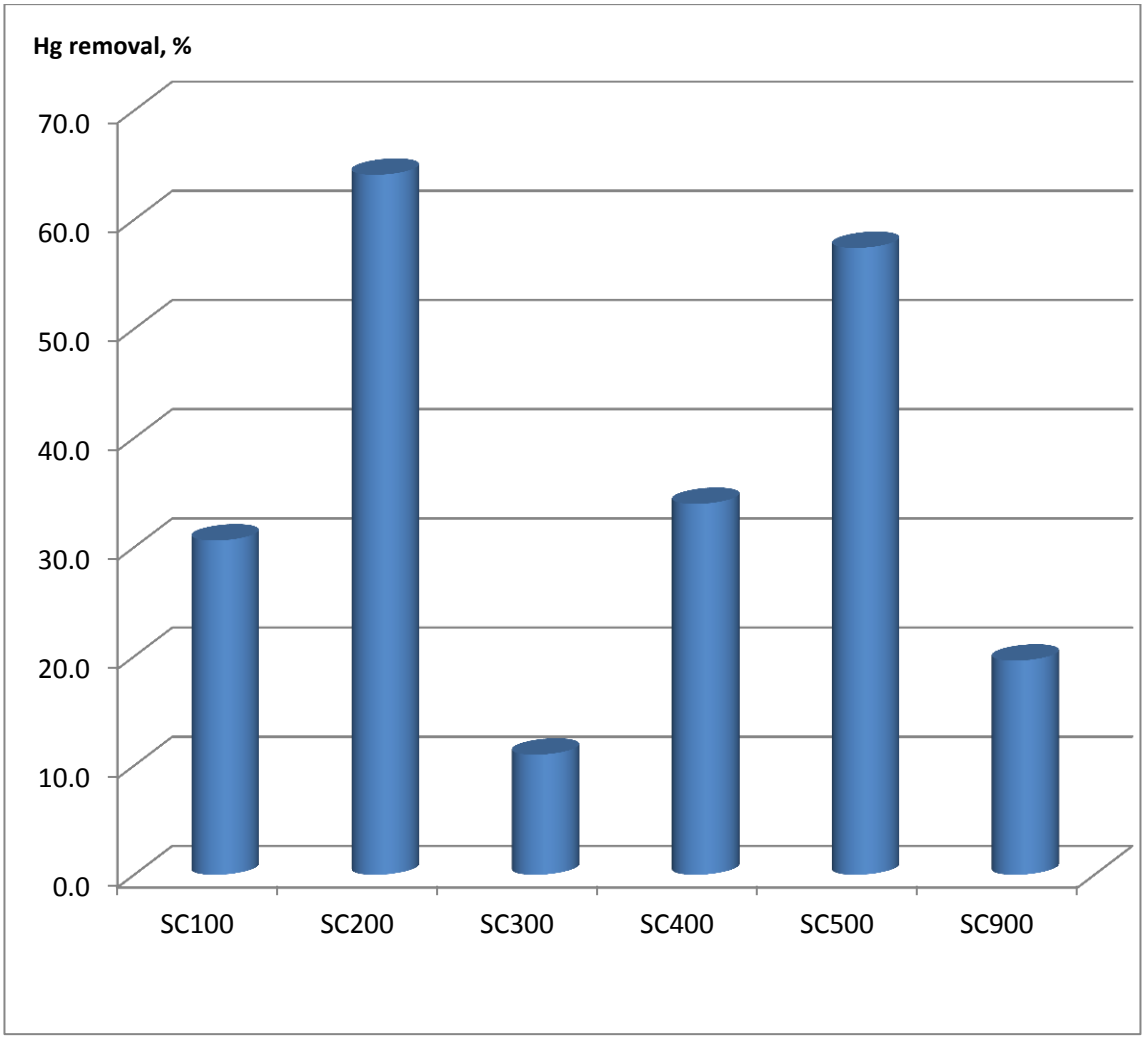


Figure 8.1 Mercury removal % of SC prepared at different temperatures

Three sulfur-carbon nanotubes prepared at 100, 500 and 1000 ºC were further evaluated, to determine their capabilities of removing different mercury species using mercury model compounds, Figure 8.3. The mercury removal increased with increasing the temperature used for sorbent preparation. This probably is due to the fact that the sulfur was homogeneously well distributed on the carbon nanotube surface at high temperature, as demonstrated in ESEM, Figures 8.4-8.6. In addition to the physical adsorbent at higher temperatures, there is a possibility of carbon sulfur bonding formation, which could improve the mercury removal efficiency. At 1100 ºC, the sulfur distribution shows very interesting patterns, indicating that there is some sort of systematic/symmetric distribution, Figure 8.4. At low temperatures there is no similar sulfur distribution pattern on the surface of the carbon nanotubes Figures 8.5, 8.6.

The ability of these sorbents to remove different mercury species are almost in the following trends: Hg^{o} > HgCl2 > mercury alkyldithiocarbamate (alkyl-Hg-TCM)> MeHgCl, which indicate that the mercury species have a great influence in the sorbent removal efficiency.

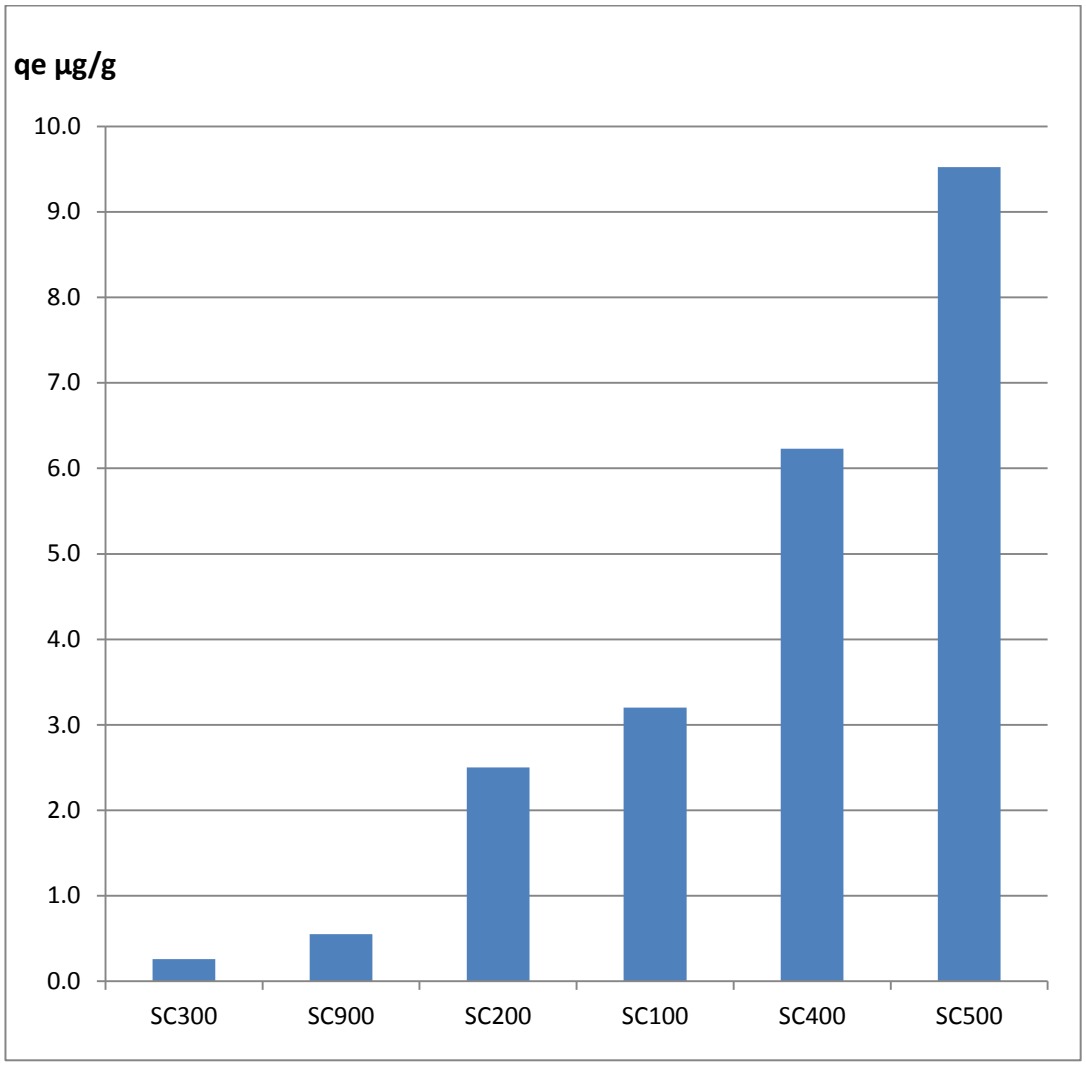


Figure 8.2. Adsorbent capacity of SC material prepared at different temperatures

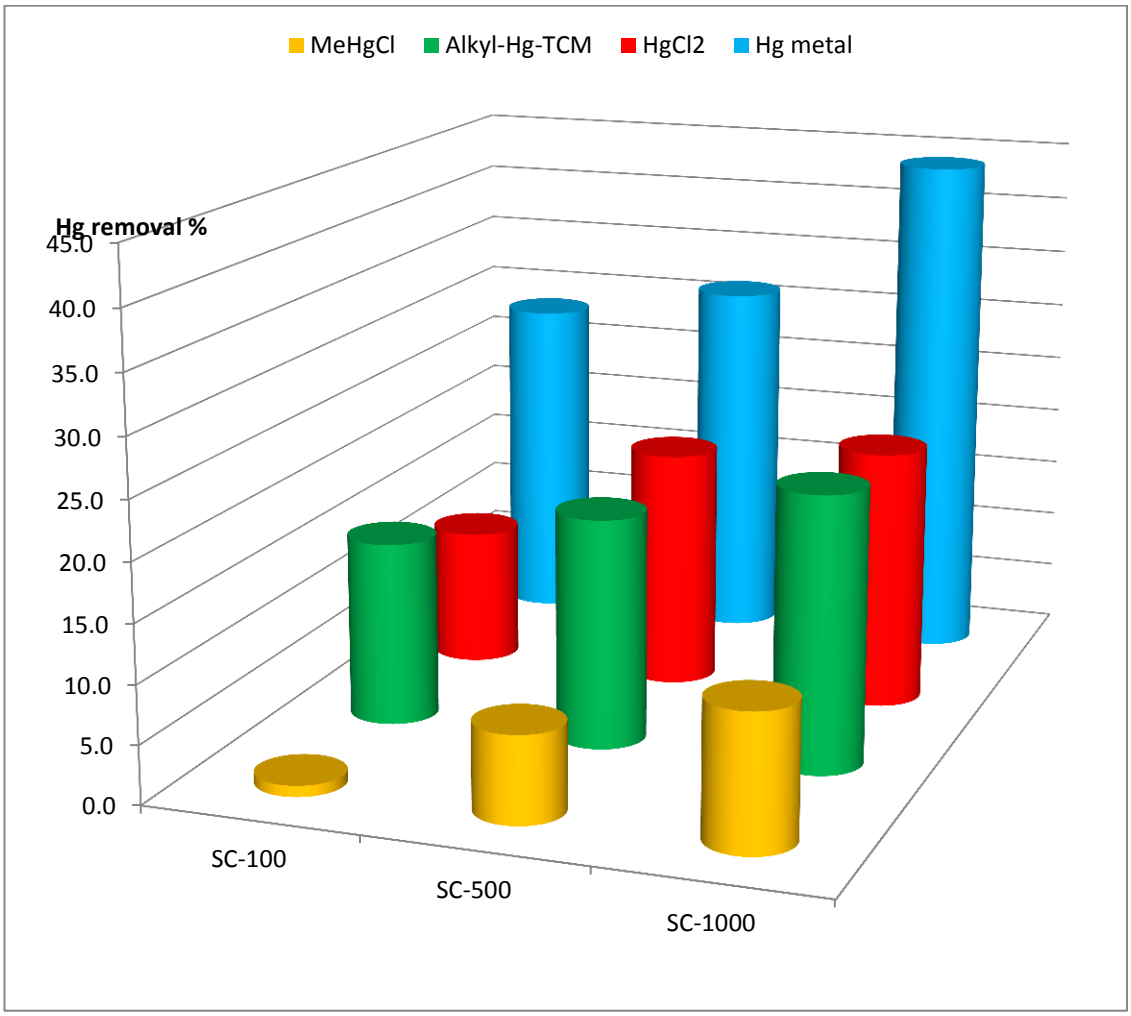


Figure 8.3. Removal % of different mercury species using SC prepared at 100, 500 and 1000 °C

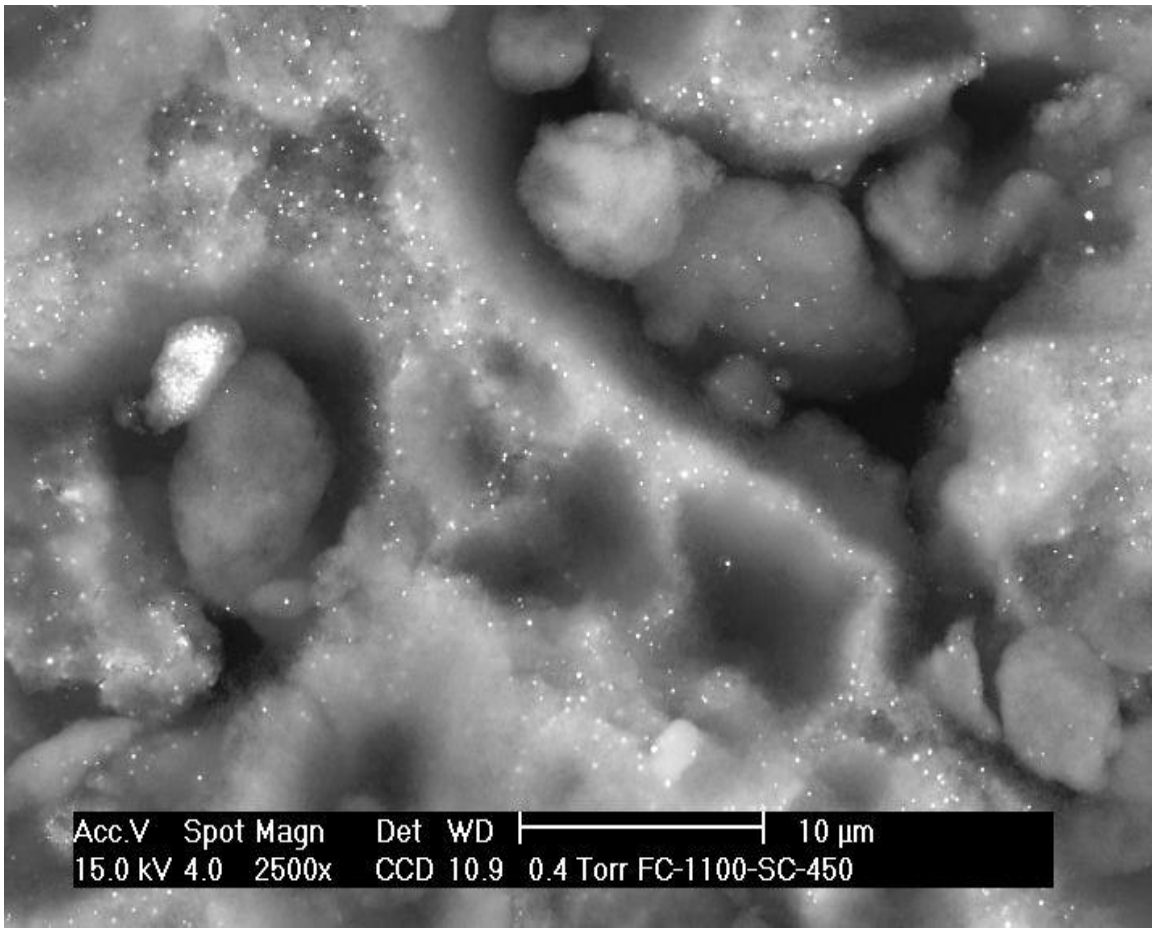


Figure 8.4 ESEM image of sulfur-carbon nanotubes prepared at 1100 °C

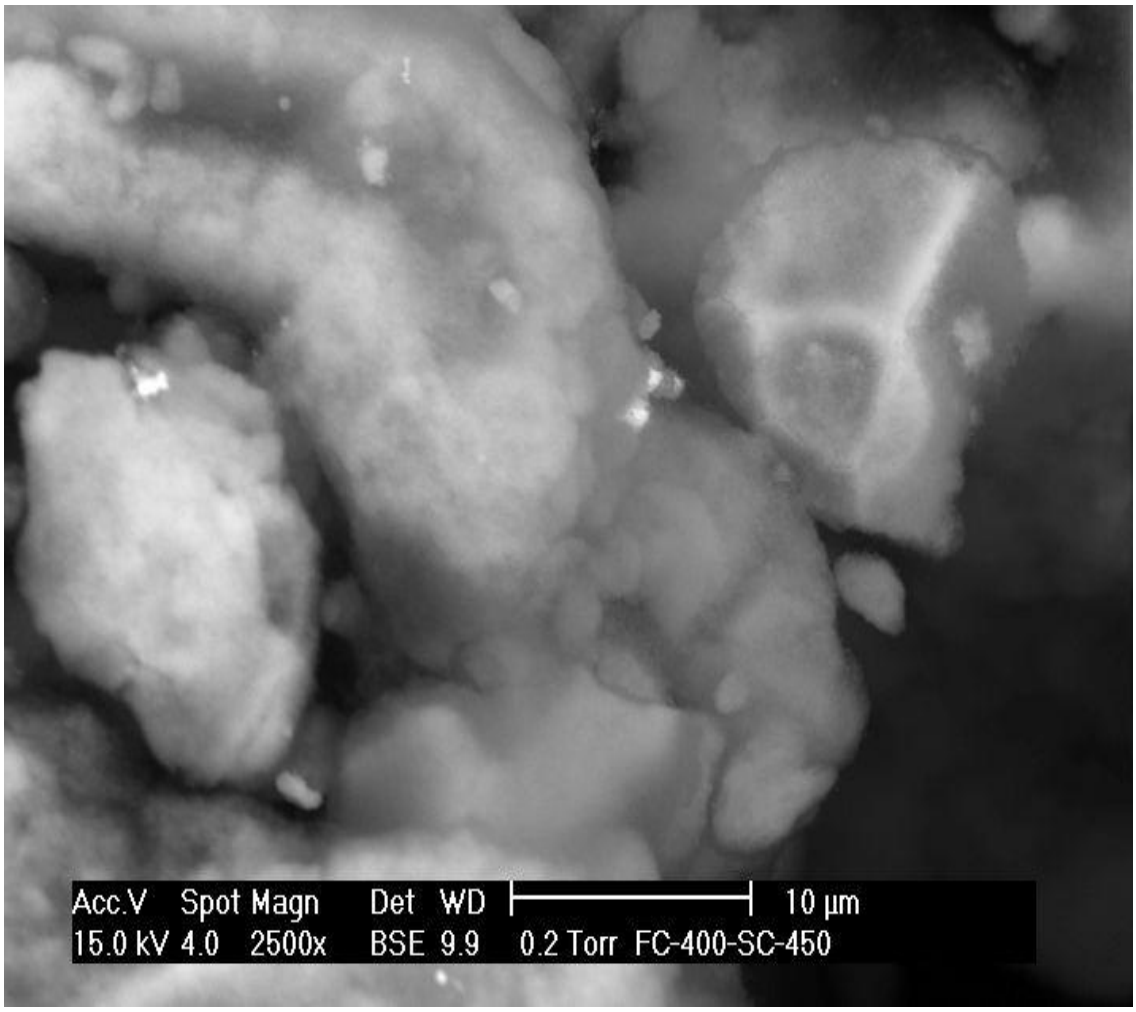


Figure 8.5 ESEM image of sulfur-carbon nanotube prepared at 400 ^{o}C

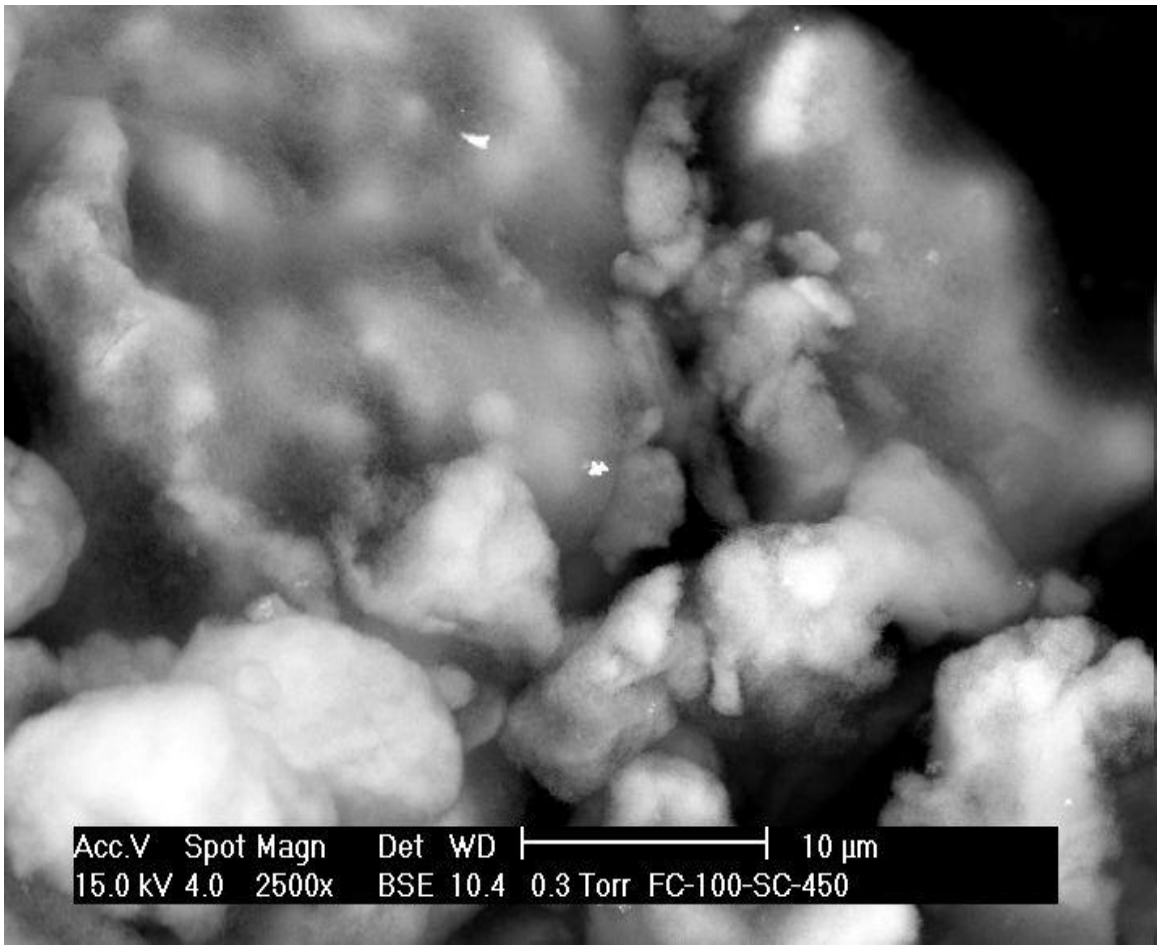
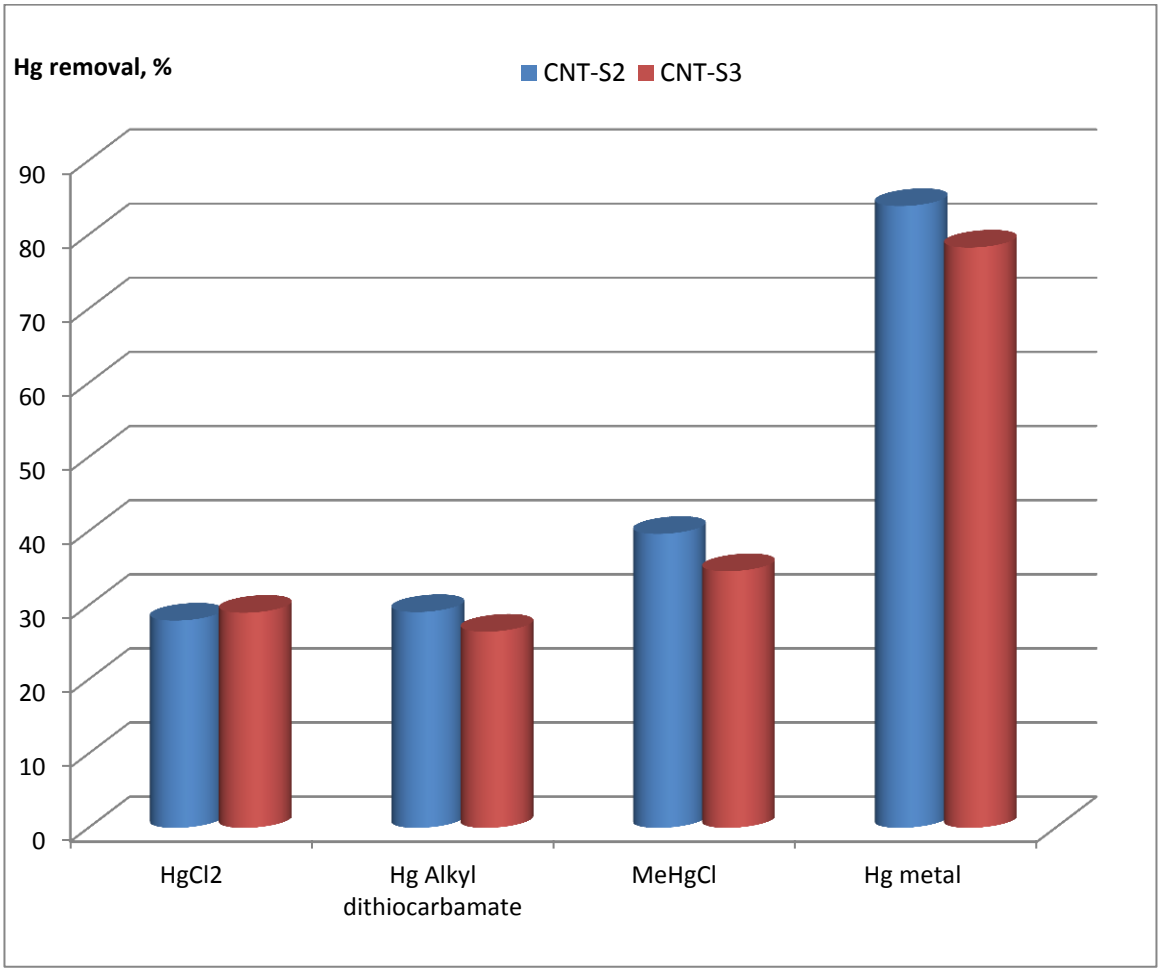


Figure 8.6 ESEM image of sulfur-carbon nanotube prepared at 100 °C

Based on the above interesting results two more samples (CNT-S2 and CNT-S3) were prepared at 700 ºC using different reaction times, two hours and three hours, and adding about 5% elemental sulfur. The results in Figure 8.7 indicate that these absorbers prepared at two and three hours made similar trends in removing various mercury species. Mercury removal efficiency of samples prepared at two hours and three hours, ranges from 28 to 84% and from about 27 to 78% respectively. The highest removal efficiency was observed using the one prepared at 2 hours, where Hg metal was about 84%. The prepared materials (CNT-S2 and CNT-S3) were compared with other sorbents in removing mercury metal, Figure 8.8. The results demonstrated that the sulfur impregnated on carbon nanotubes provided better mercury removal performance. CNT-S2 and CNT-S3 exceeded even the elemental sulfur in removing mercury metal. This is probably due to the good distribution of elemental sulfur over a high surface area provided by the carbon nanotubes.



Figurer 8.7. Removing different mercury species using CNT-S2 and CNT-S3 prepared at two and three hours

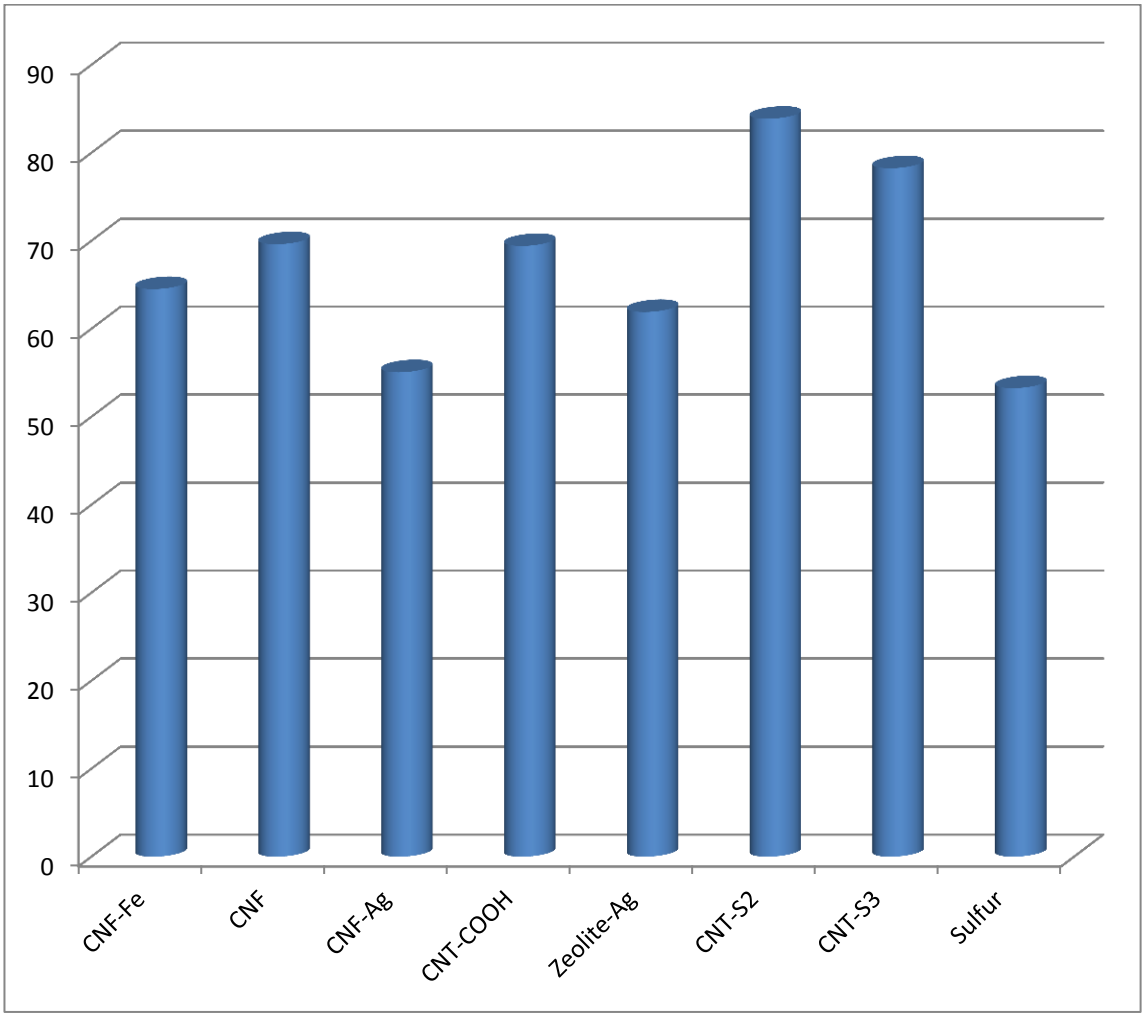


Figure 8.8. Comparison of different sorbents efficiencies of removing Hg metal

8.2 CHARACTERIZATION OF CNT-S2 AND CNT-S3

The idea of reacting sulfur with carbon nanotubes was triggered by employing the high reactivity of elemental sulfur with mercury species, particularly elemental mercury. Just impregnating the sulfur on the carbon nanotube physically for liquid hydrocarbon applications will not help much, as the sulfur will probably be leaching with time, resulting in product contamination. A literature survey indicated that there were few publications addressing the sulfur impregnated process on carbon nanotubes, for the development of composite cathode for lithium/ sulfur batteries [96-99].

This work addressed the need of making sulfur-carbon nanotube chemical bonding to eliminate any migration of sulfur to the hydrocarbon streams and also to make very stable mercury/sulfur complexes. The results of using such a concept were very promising as indicated earlier and therefore the following sections will address the characterization of these composites.

The carbon nanotube and sulfur/carbon nanotube prepared at 700 ºC and two and three hours reaction time were subjected to XRD evaluation, Figures 8.9-8.11, these samples were labeled as CNT-S2 and CNT-S3. Figure 8.9 shows XRD carbon nanotubes spectra, which are typical of CNT spectra. Figure 8.10 shows XRD spectra of the product after three hours reaction time which resulted in the formation of carbon sulfur chemical bonding. Some NiS_2 was also detected and this most probably due to some contamination taking place during the CNT preparation. XRD spectra of the sample prepared at three hours consists of

carbon nanotubes and carbon disulfide (CS_2), and did not show any evidence of an elemental sulfur peak, indicating that most of the elemental sulfur was consumed.

Figure 8.11 is the XRD spectra of the sample prepared at two hours indicates that there is no formation of carbon sulfur bond CS_2. The sample consists mainly of elemental sulfur (S_8) with carbon nanotubes, in which the peaks of elemental sulfur are very strong. There was no evidence of any NiS peak in the sample prepared at two hours, which is a very interesting observation. It seems that the Nickel acts as a catalyst, helping the chemical bond formation between the elemental sulfur carbon nanotubes. Also seems that the NiS formation has great influence in removing mercury. High temperatures may result in the deformation or damaging of the CNTs however, the purpose of such combination of elemental sulfur and CNTs is the performance of resulted sorbent to remove mercury. Such observations require more technical investigation, which will not be addressed in this study.

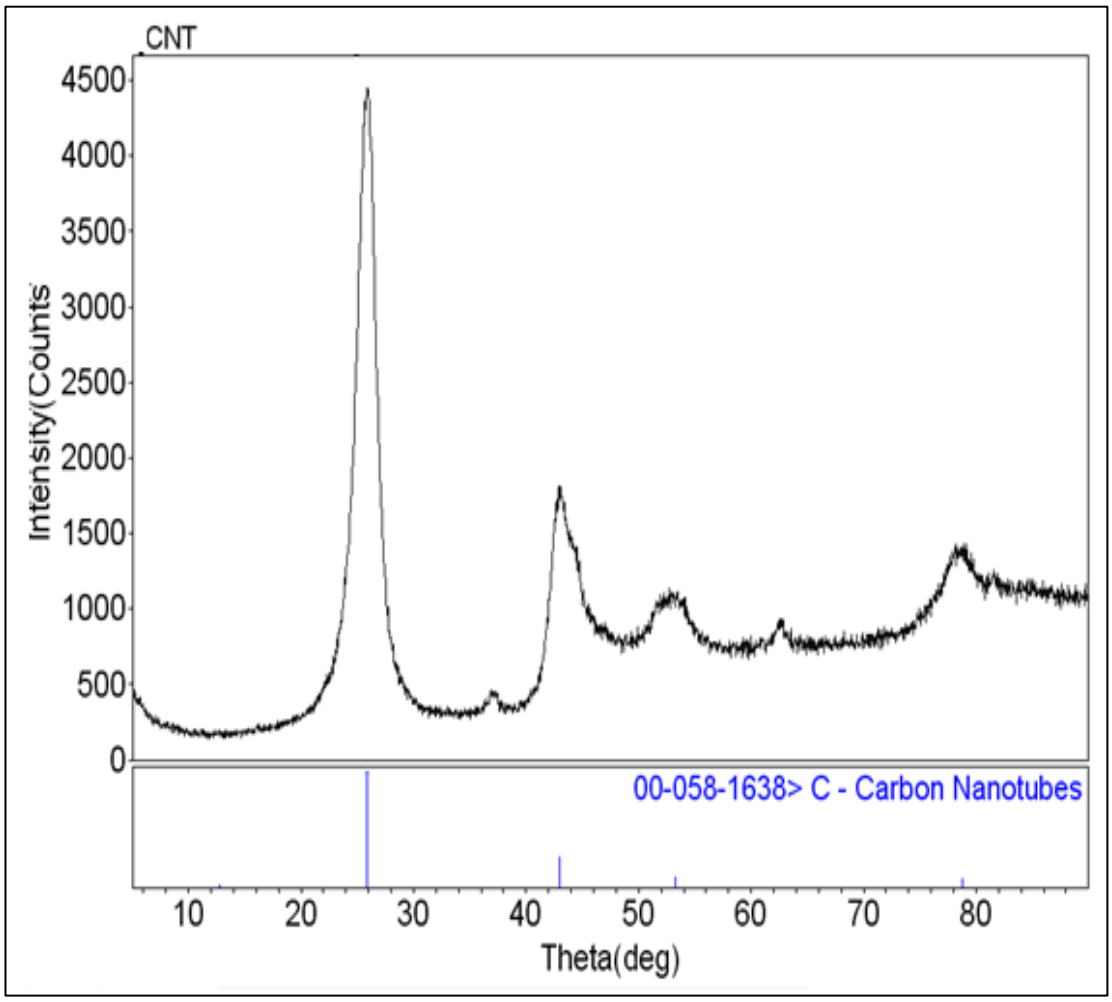


Figure 8.9 XRD for carbon nanotubes

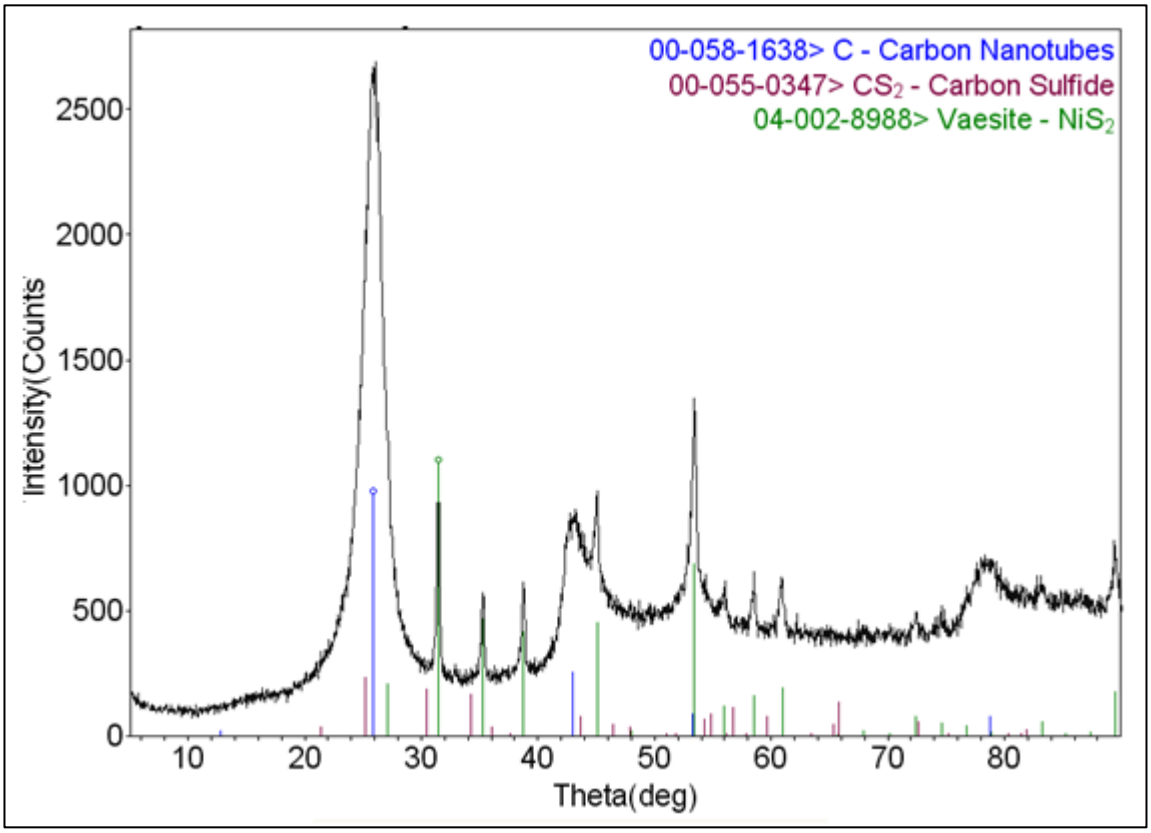


Figure 8.10 XRD Spectra of CNT-S3 prepared at 3 hours.

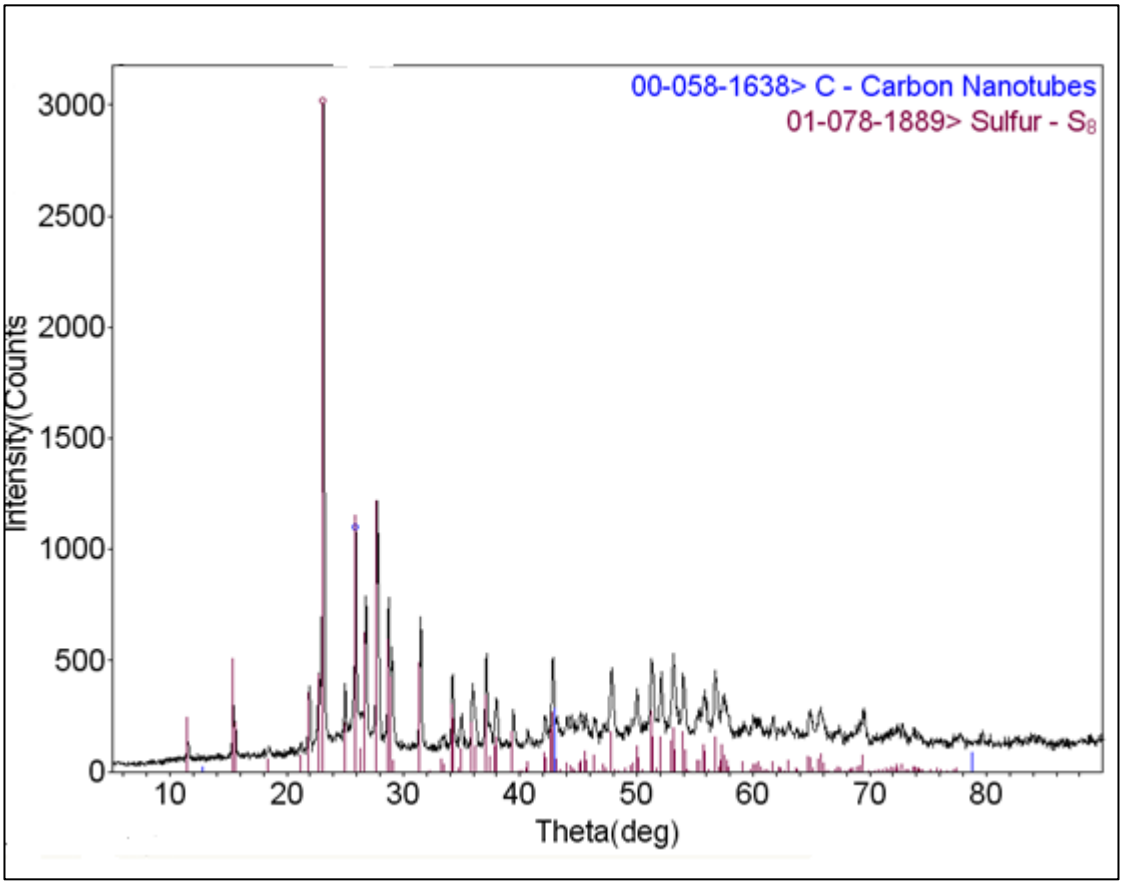


Figure 8.11 XRD of CNT-S2 prepared at two hours.

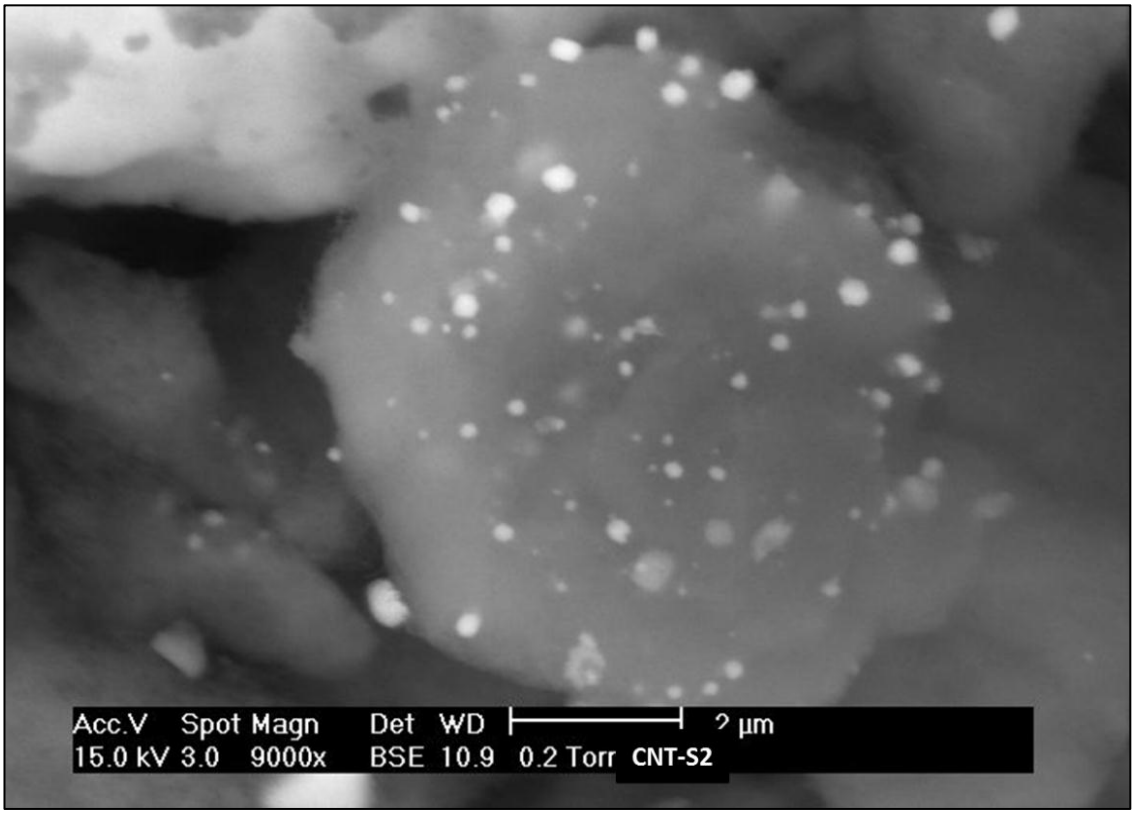


Figure 8.12 ESEM image of sulfur-carbon nanotube prepared at 2 hours

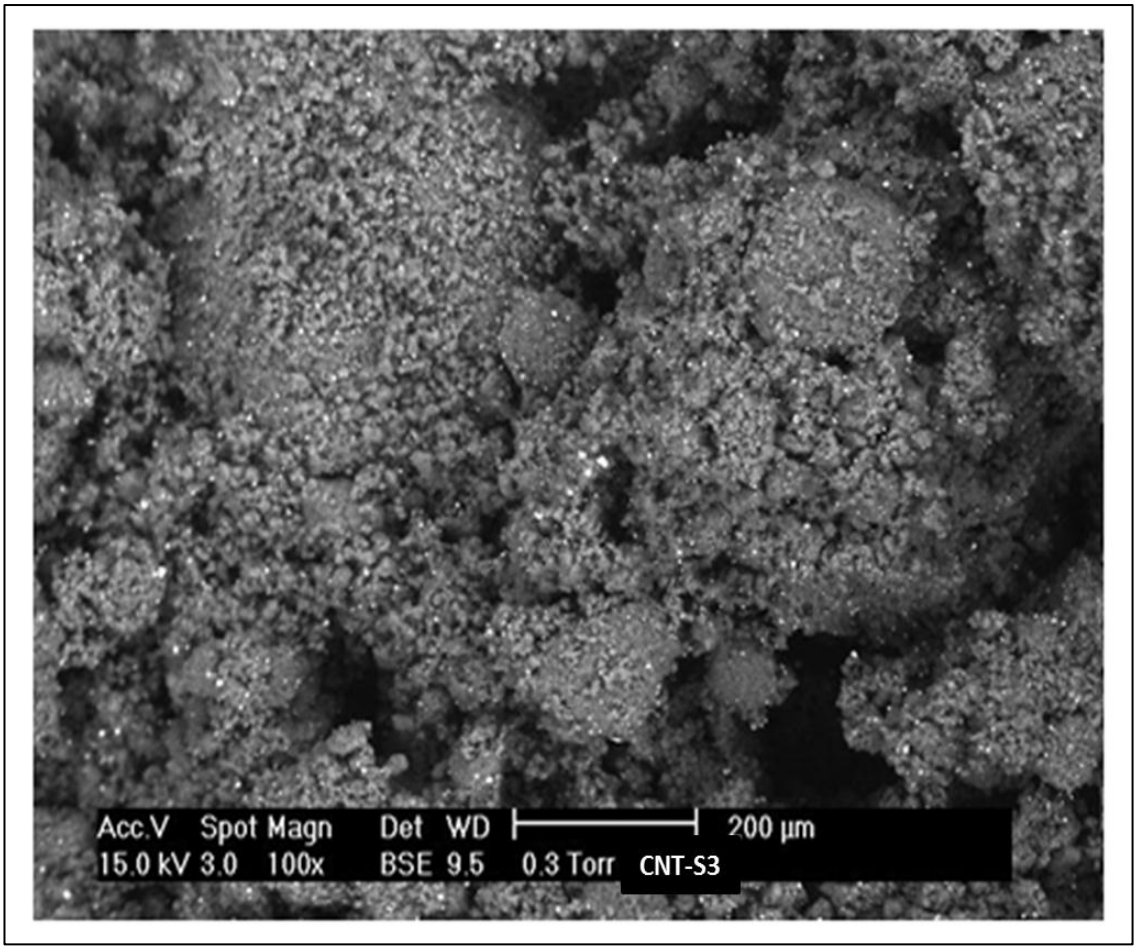


Figure 8.13 ESEM image of sulfur-carbon nanotube prepared at 3 hours

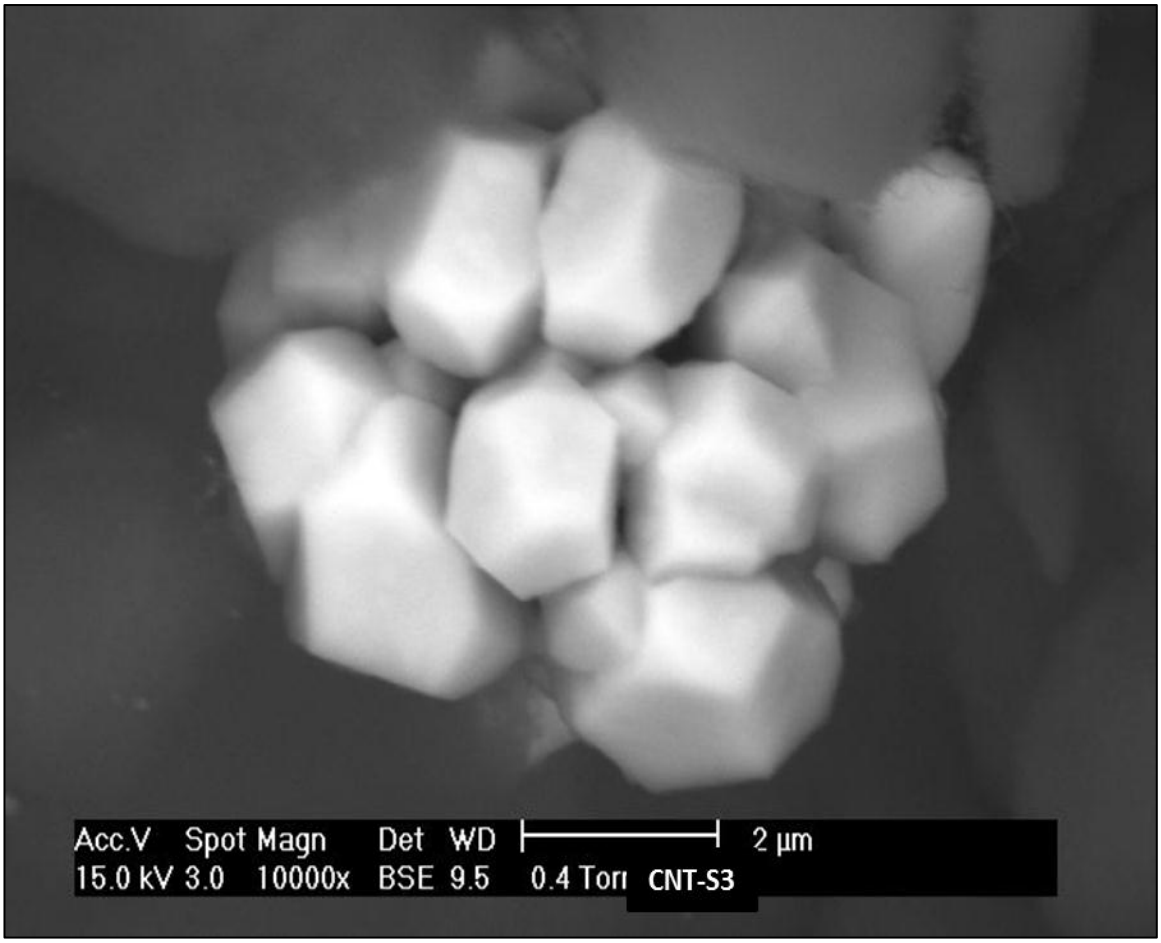


Figure 8.14 ESEM of CNT-S3 prepared at three hours

8.3 CONCLUSION

The combination of elemental sulfur and CNT was explored to develop new sorbent utilizing the high reactivity of elemental sulfur with mercury species, particularly elemental mercury. The results are very promising and these sorbents can be used for mercury removal. The findings also indicated that under certain condition there are a possibility chemical bond formed between the sulfur and CNT and this was explored and tested for mercury removal. Making such sorbents based on chemical bonds not only on physical interaction is considered to be a new innovative approach to remove mercury from liquid hydrocarbon due to the high stability. Such sorbents can be used to remove mercury from water, gas and liquid hydrocarbons. However, requires more investigation to assist this approach and characterize the formation of the sulfur –CNT chemical bond formation.

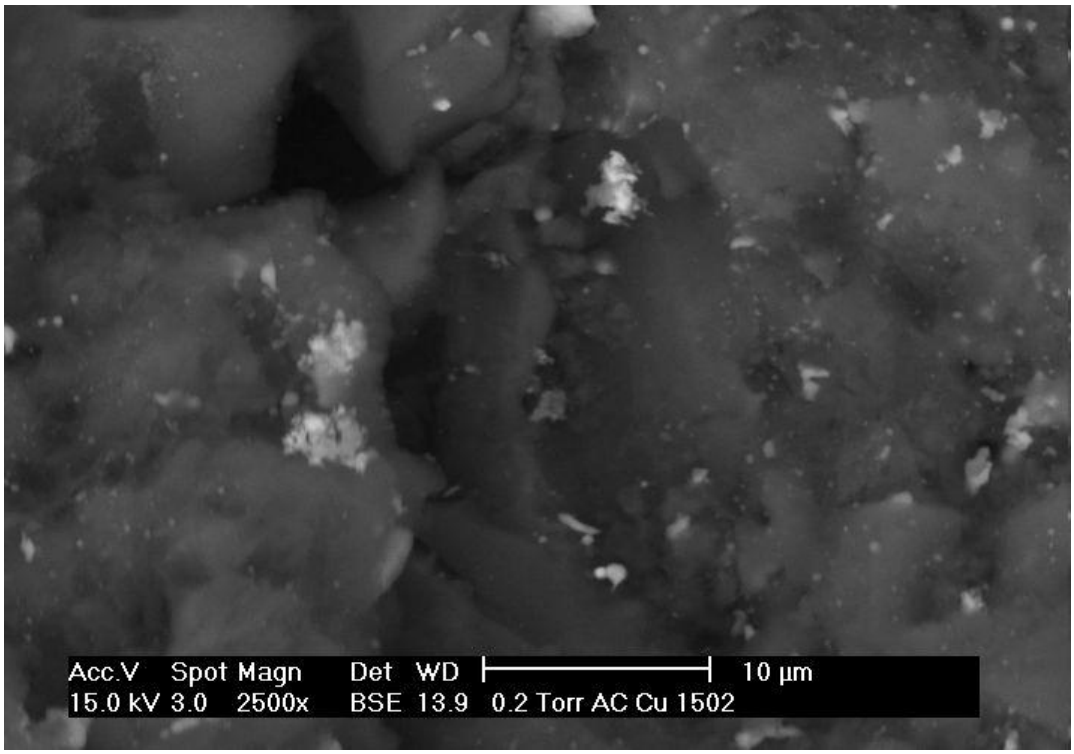
8.4 FUTURE WORK

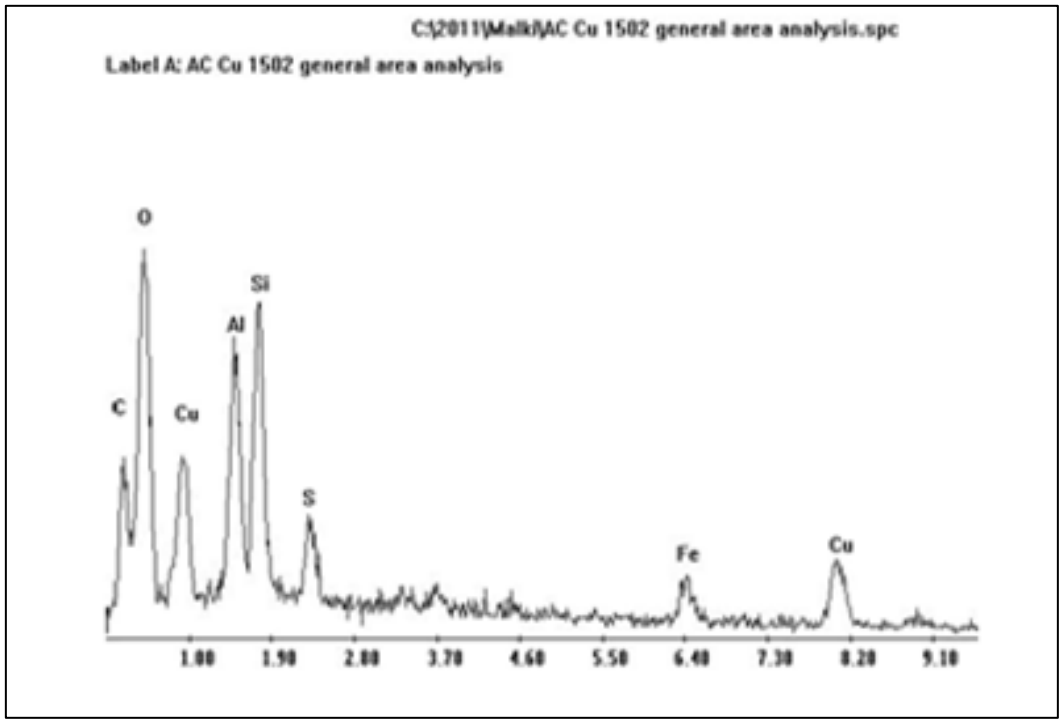
The preparation method of impregnating elemental sulfur with CNTs, CNFs and activated carbon will be deep evaluated. The chemical reaction that took place between the CNT and elemental sulfur will be also investigated in more details. The sorbent will be evaluated for removing mercury from water, gas and liquid hydrocarbons.

APPENDIX I

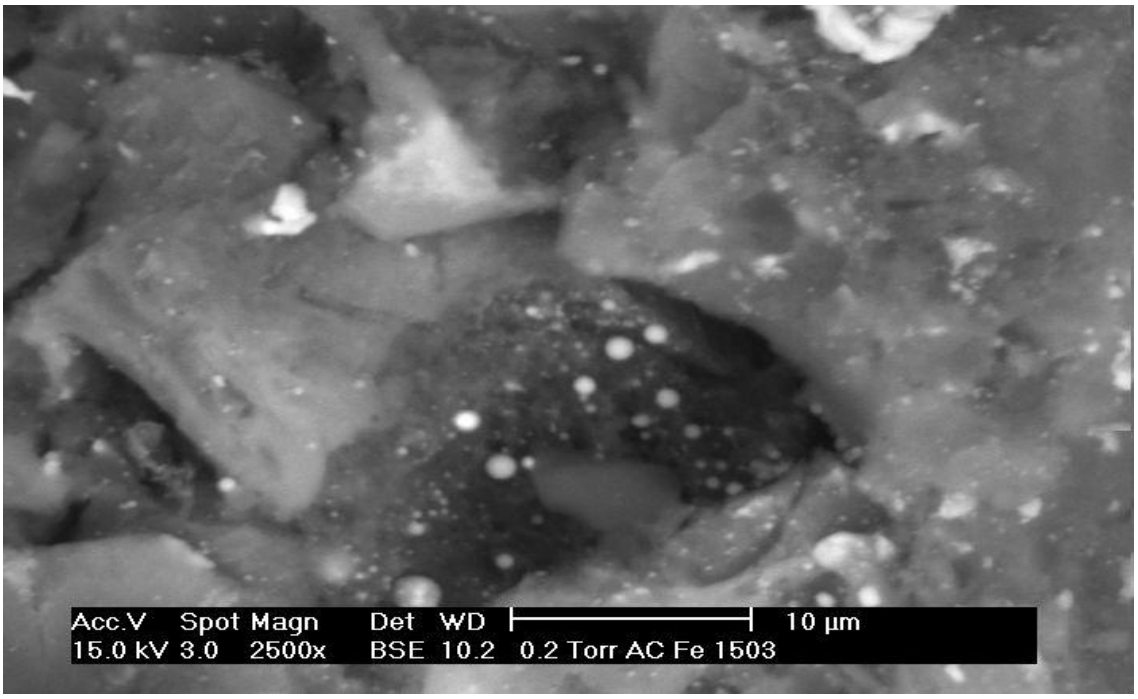
ESEM AND EDX OF SORBENTS

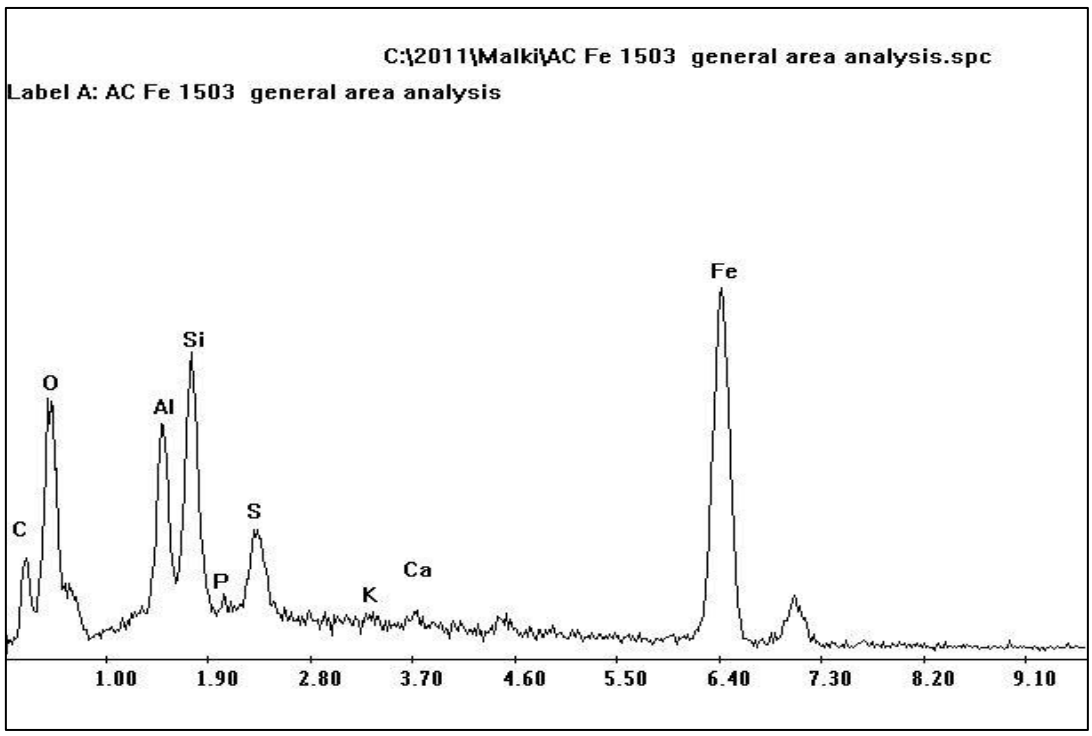
ESEM and EDX of Activated Carbon with Copper



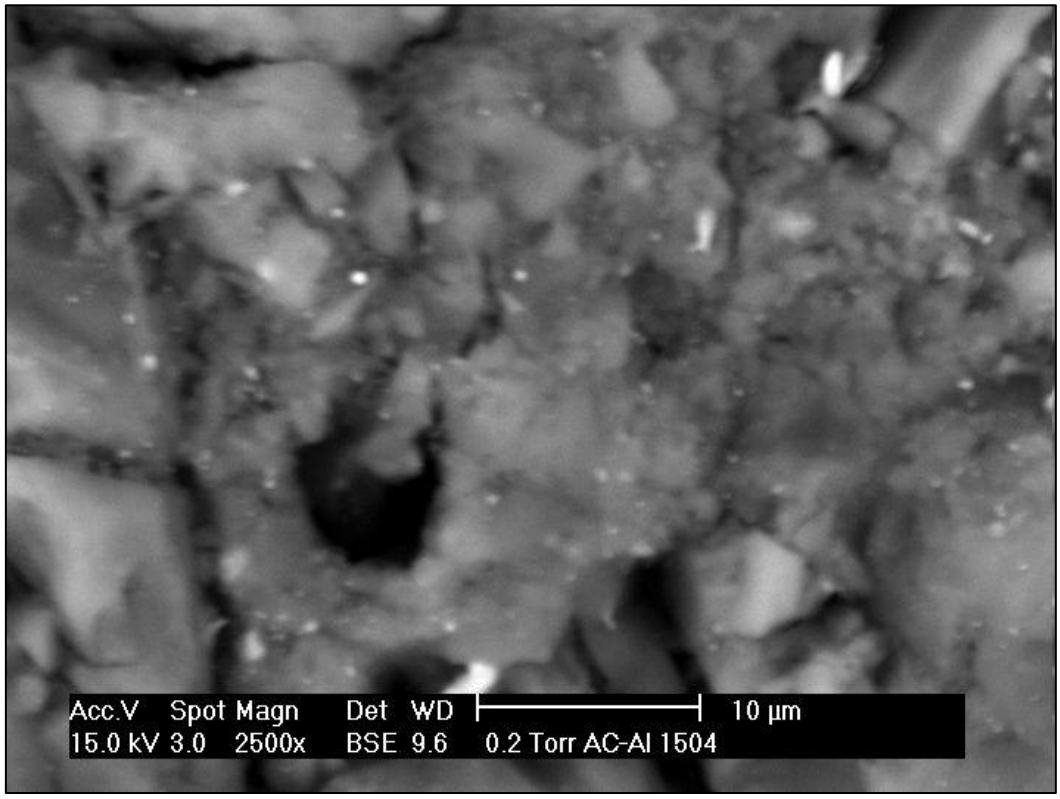


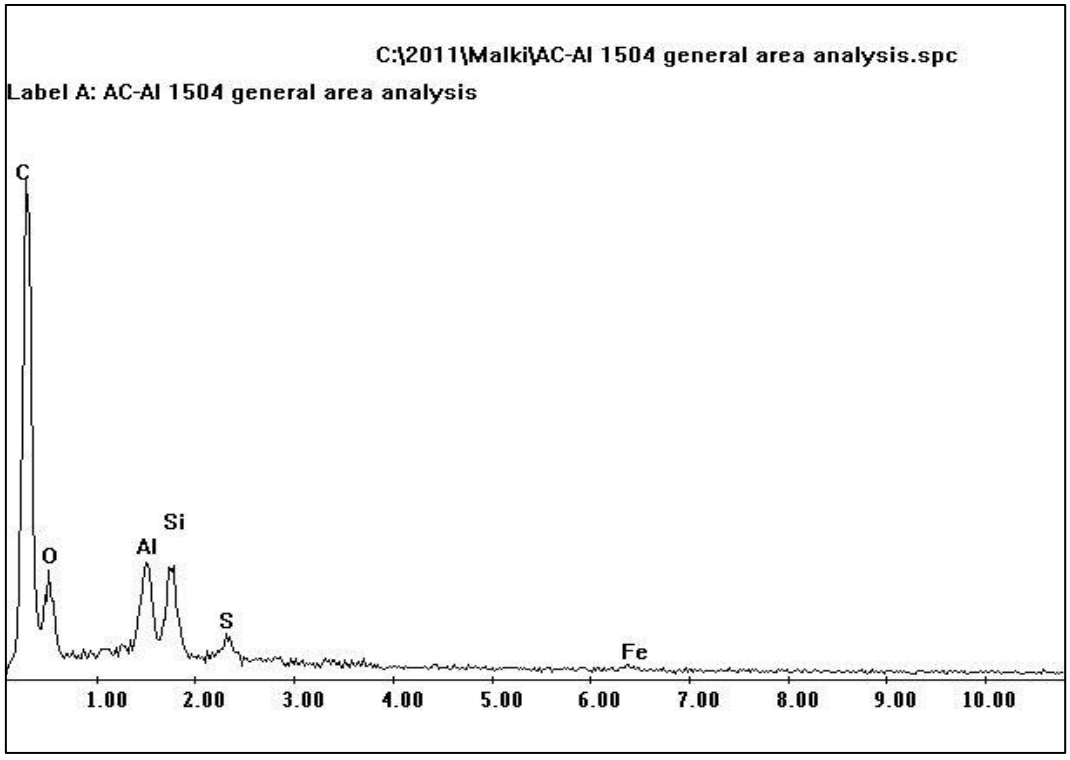
ESEM and EDX of Activated Carbon with Iron



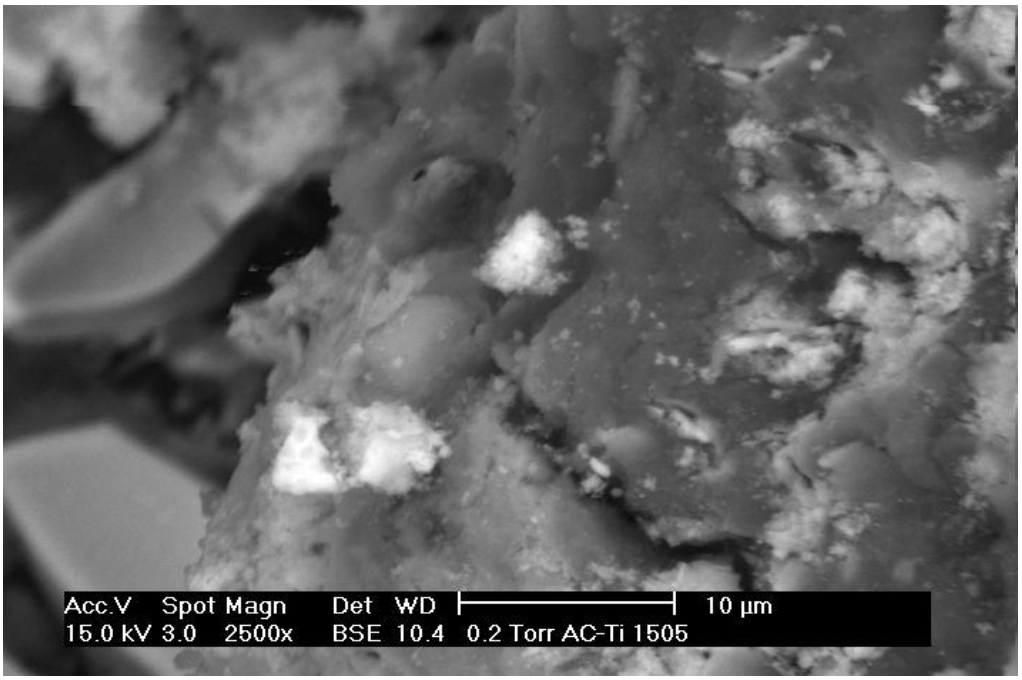


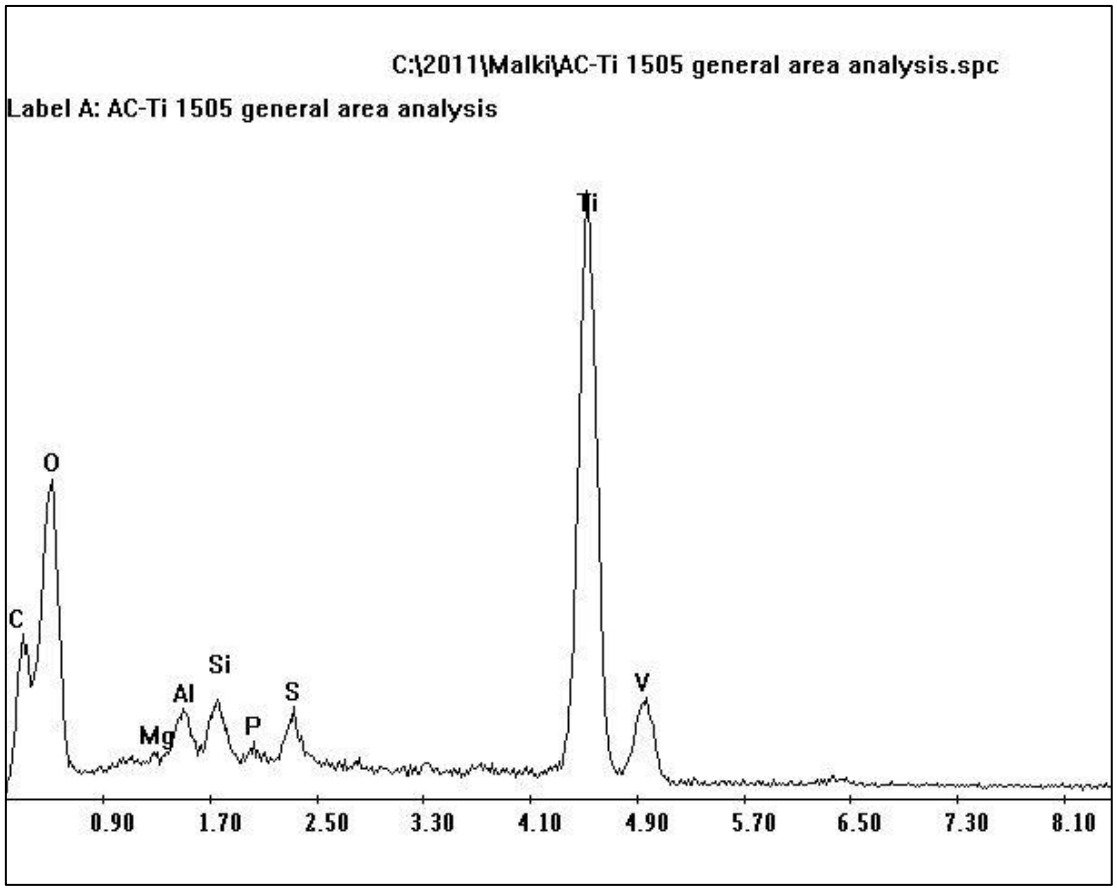
ESEM and EDX of Activated Carbon with Al



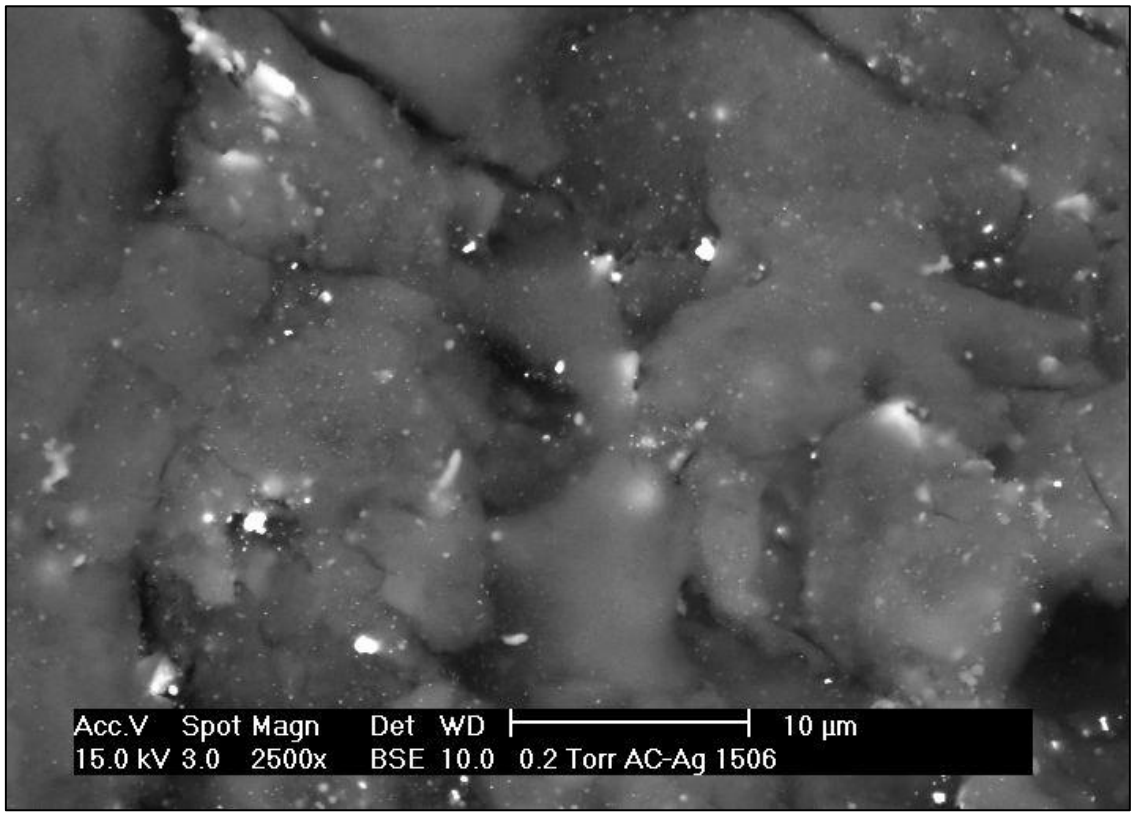


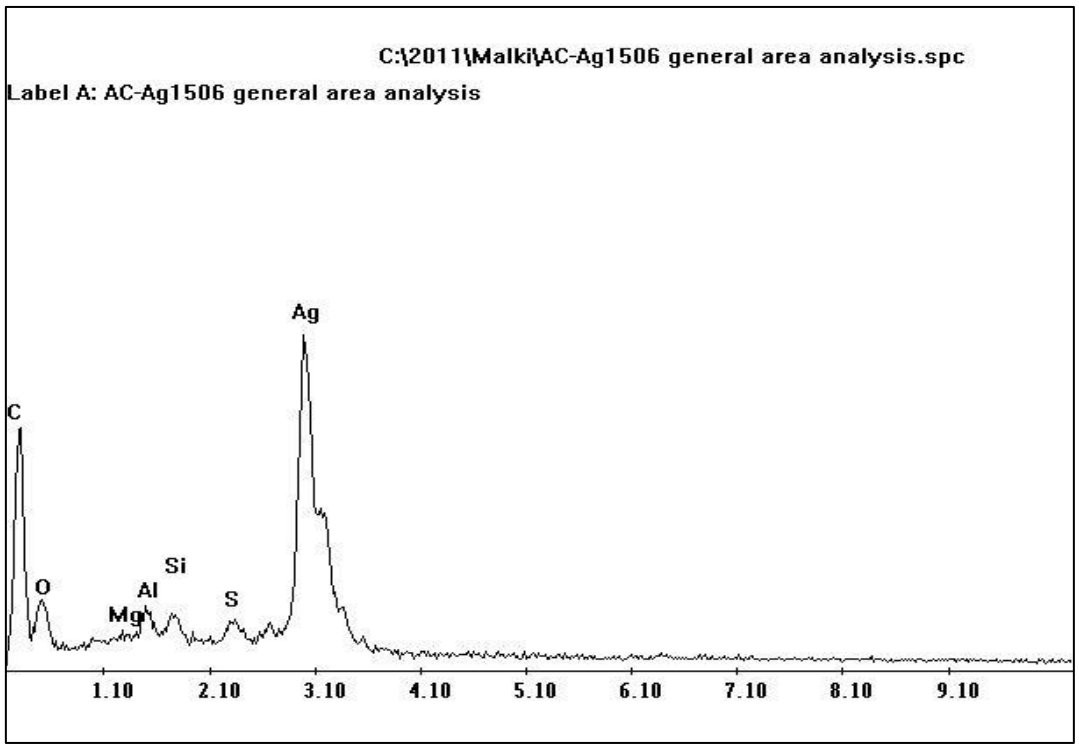
ESEM and EDX of Activated carbon with Titanium



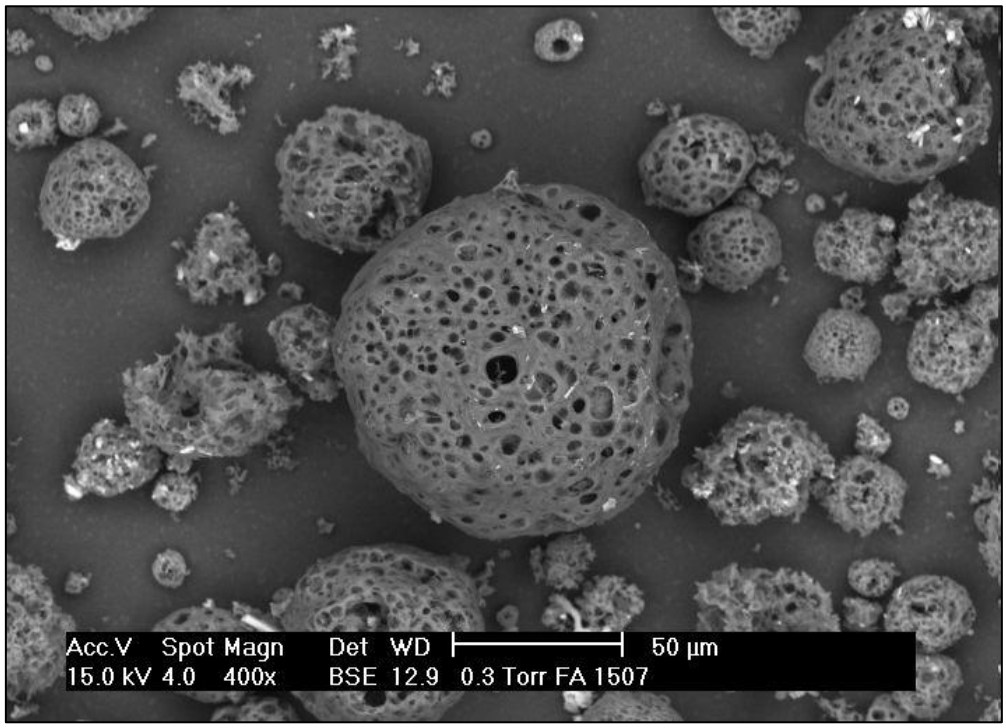


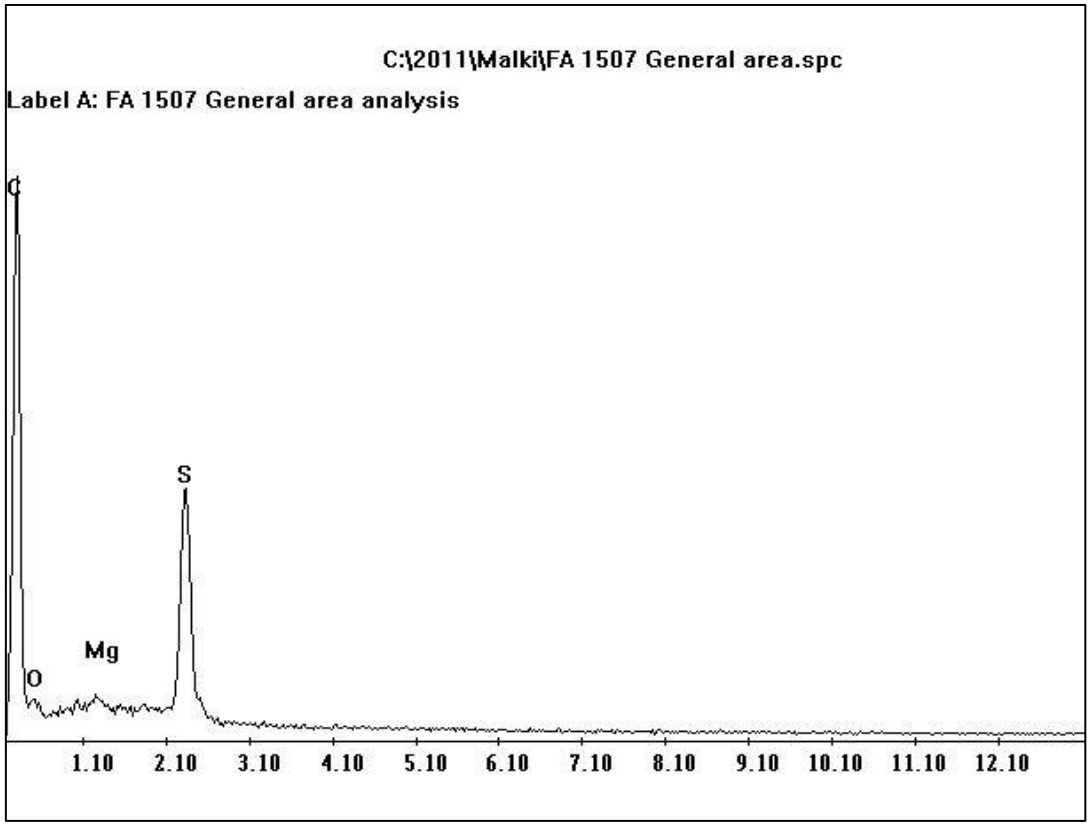
ESEM and EDX of Activated Carbon with Silver



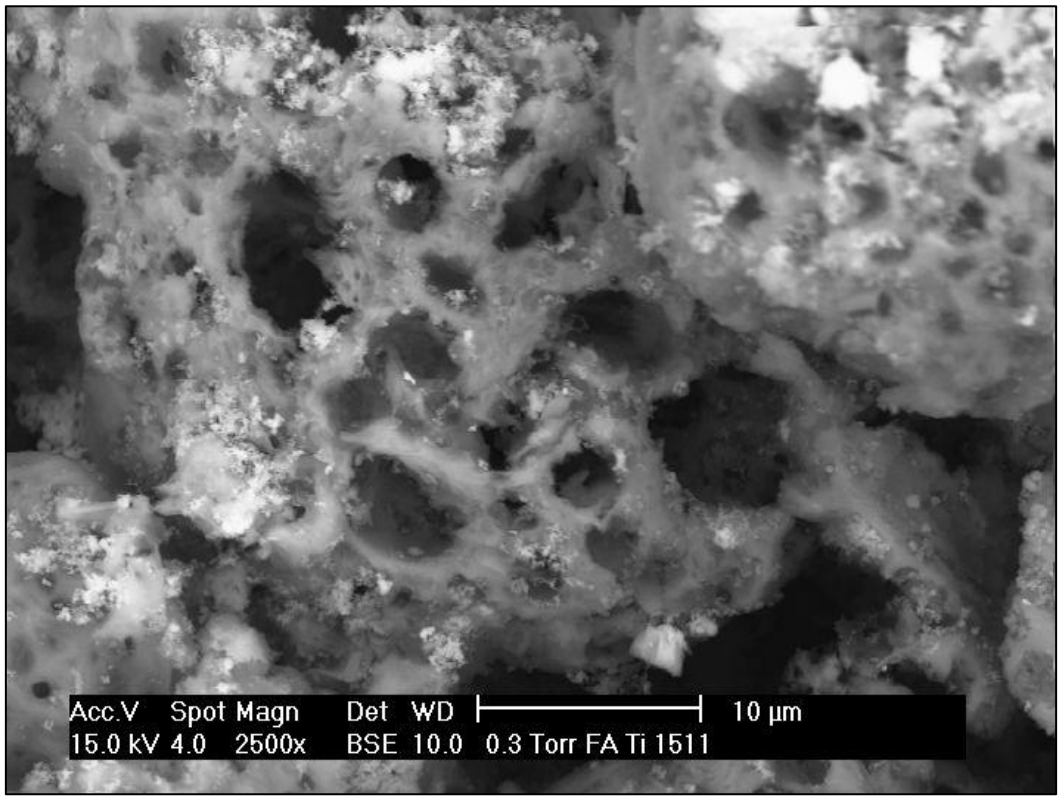


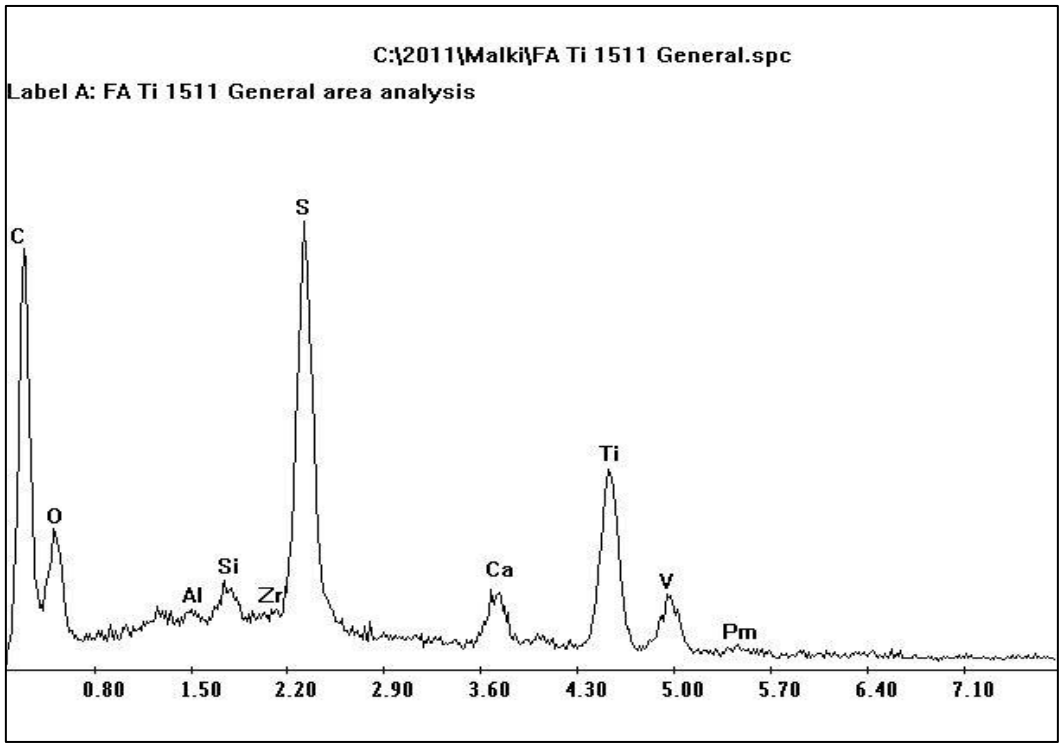
ESEM and EDX of Fly Ash



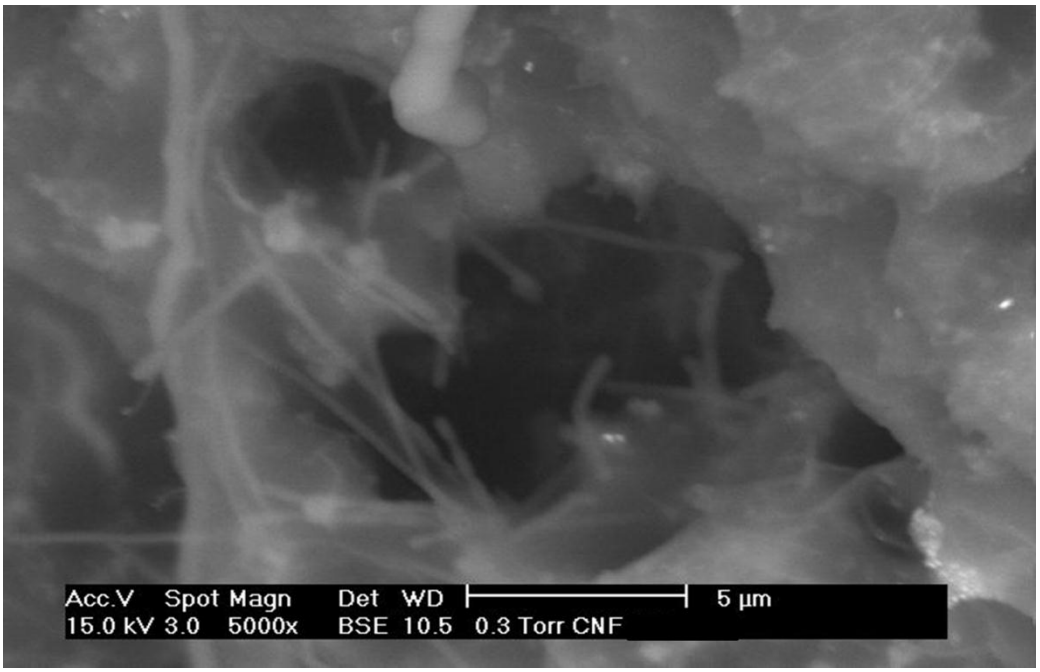


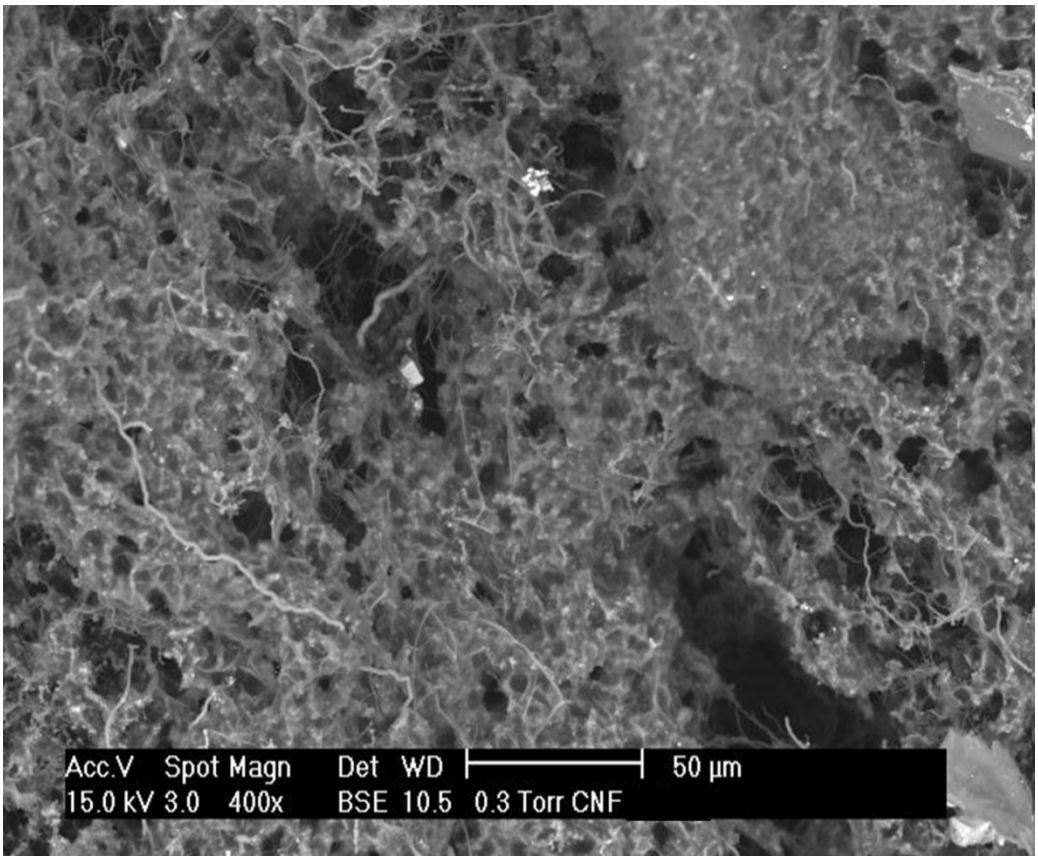
ESEM and EDX of Fly Ash with Titanium



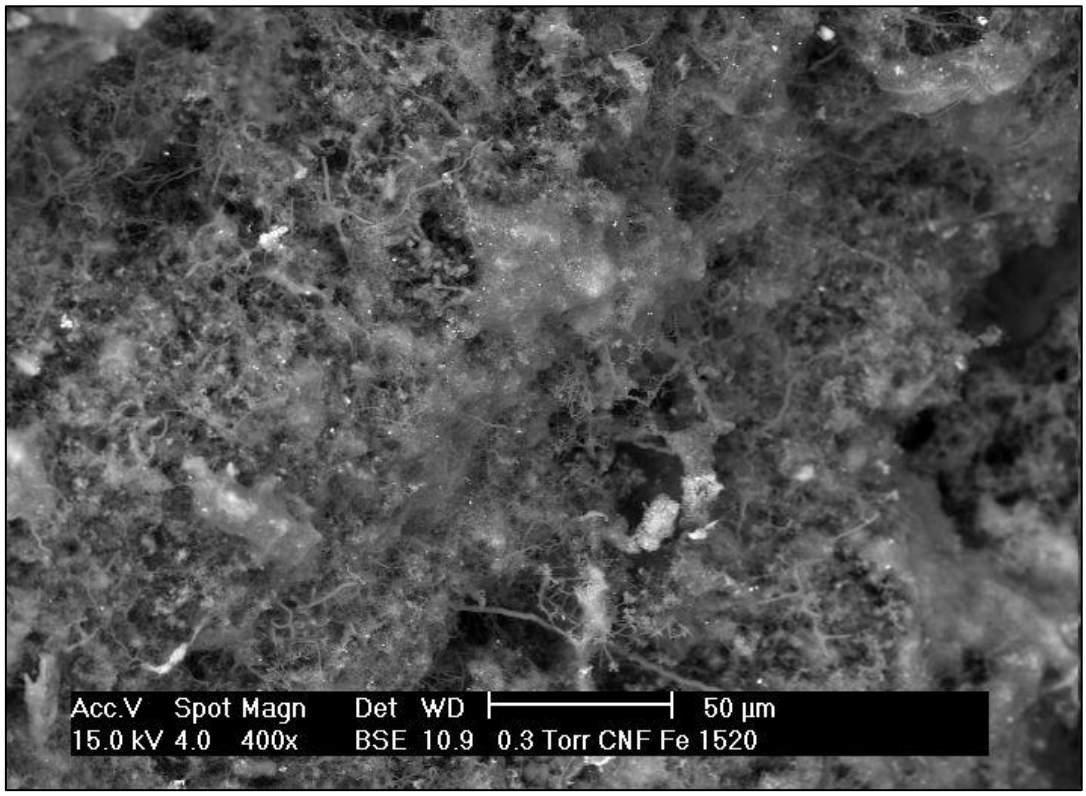


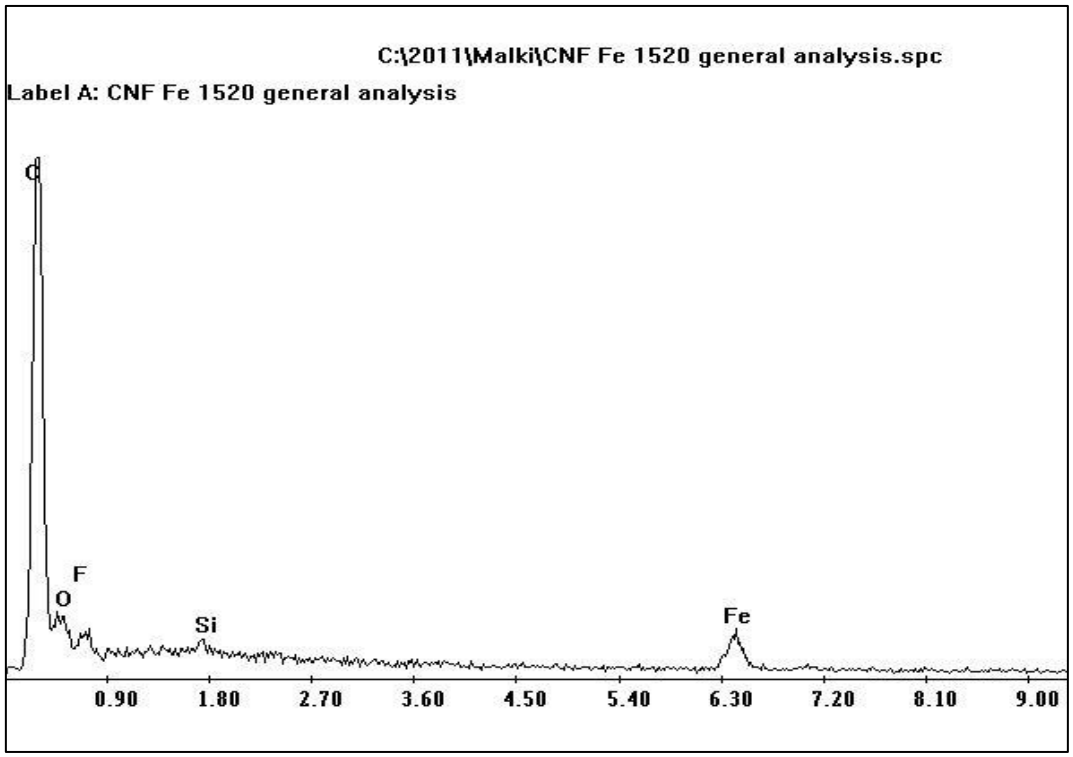
ESEM of Carbon Nanofibers



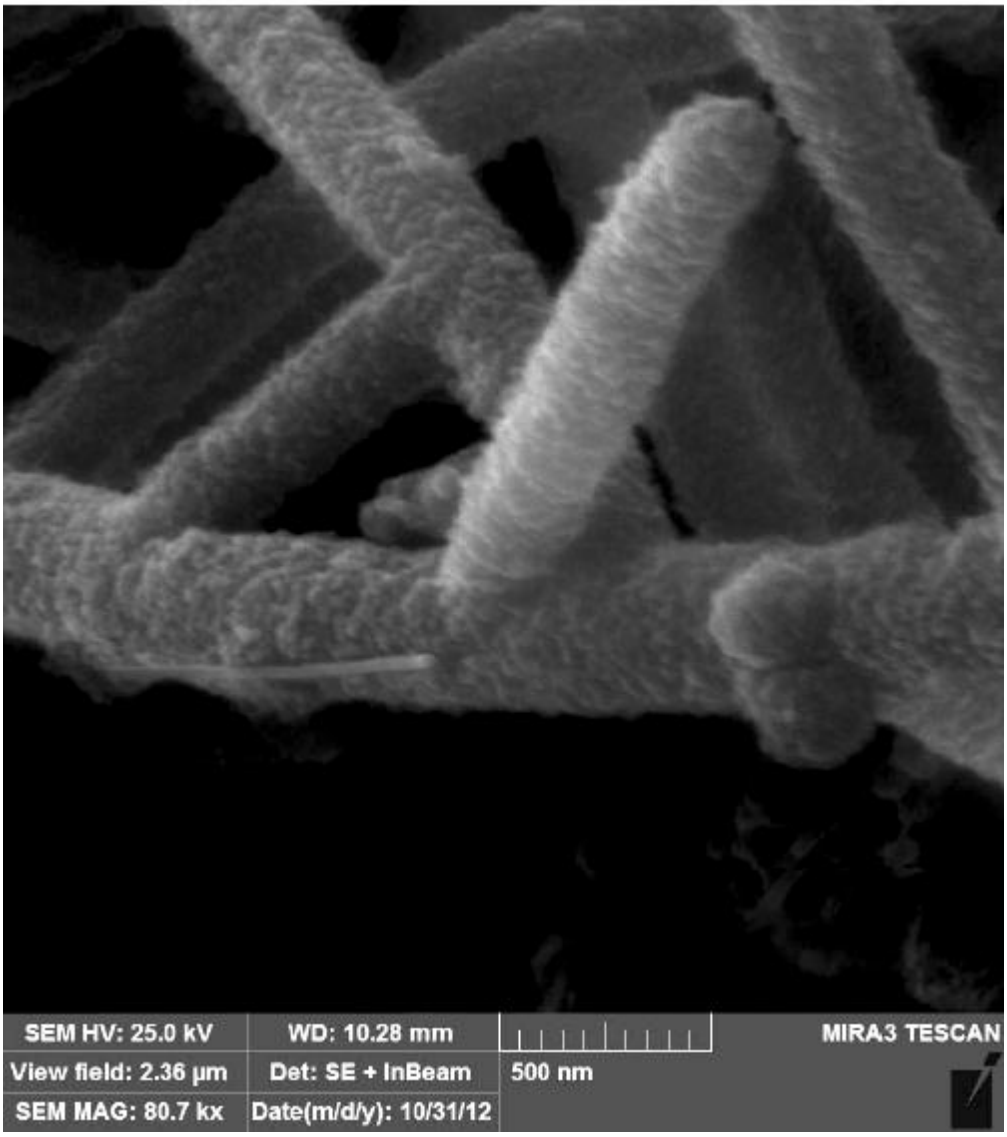


ESEM and EDX of Carbon Nanofibers with Fe

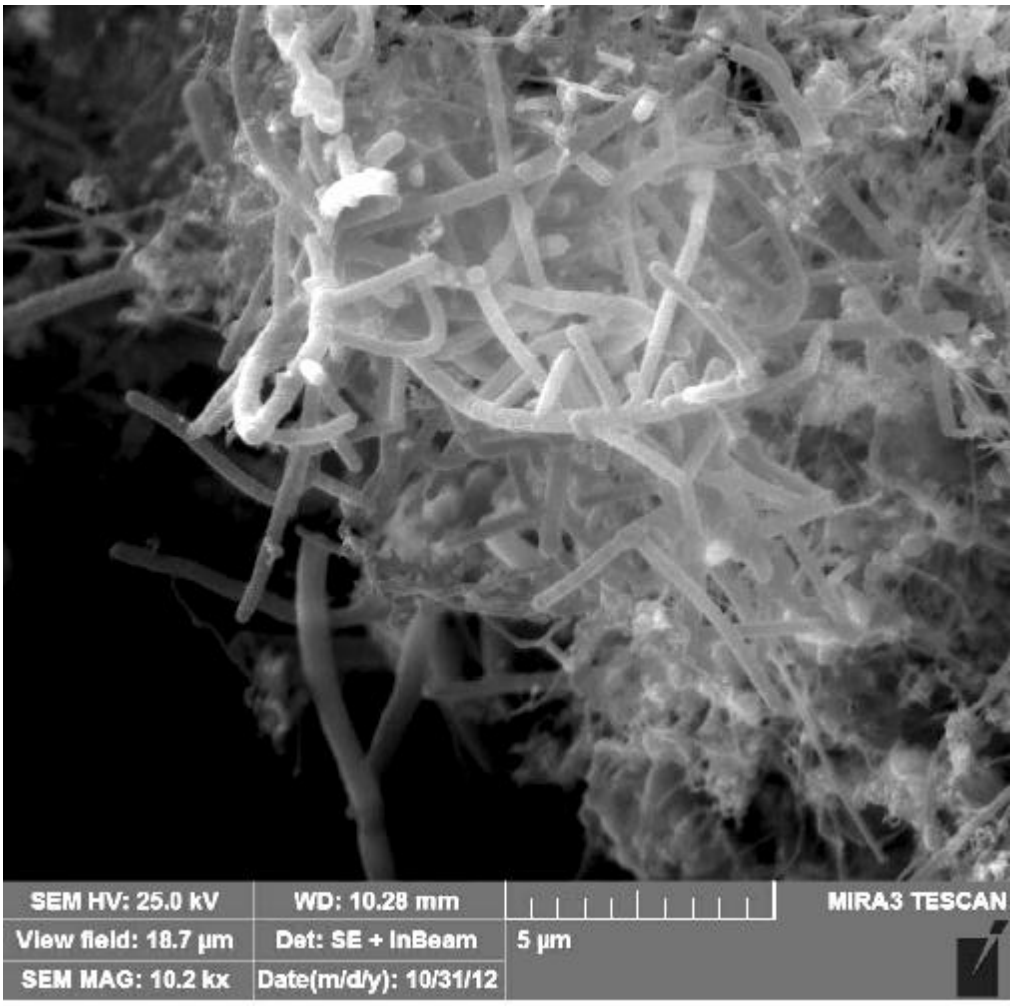




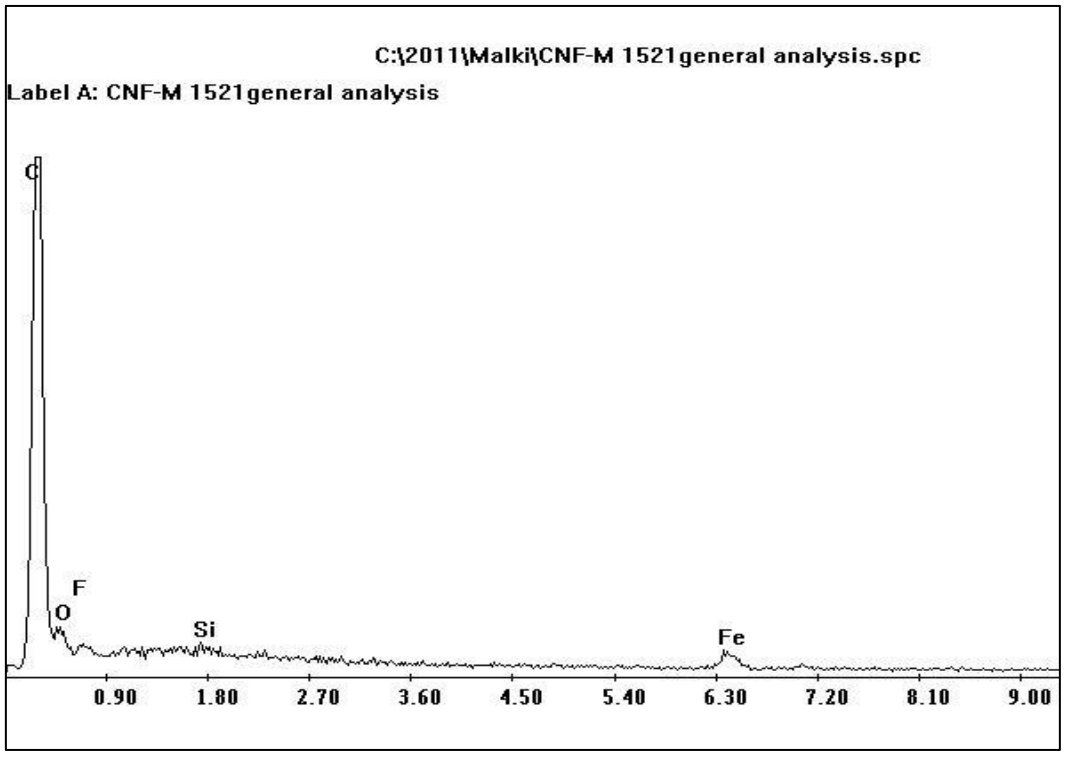
ESEM of Carbon Nanofibers with Al



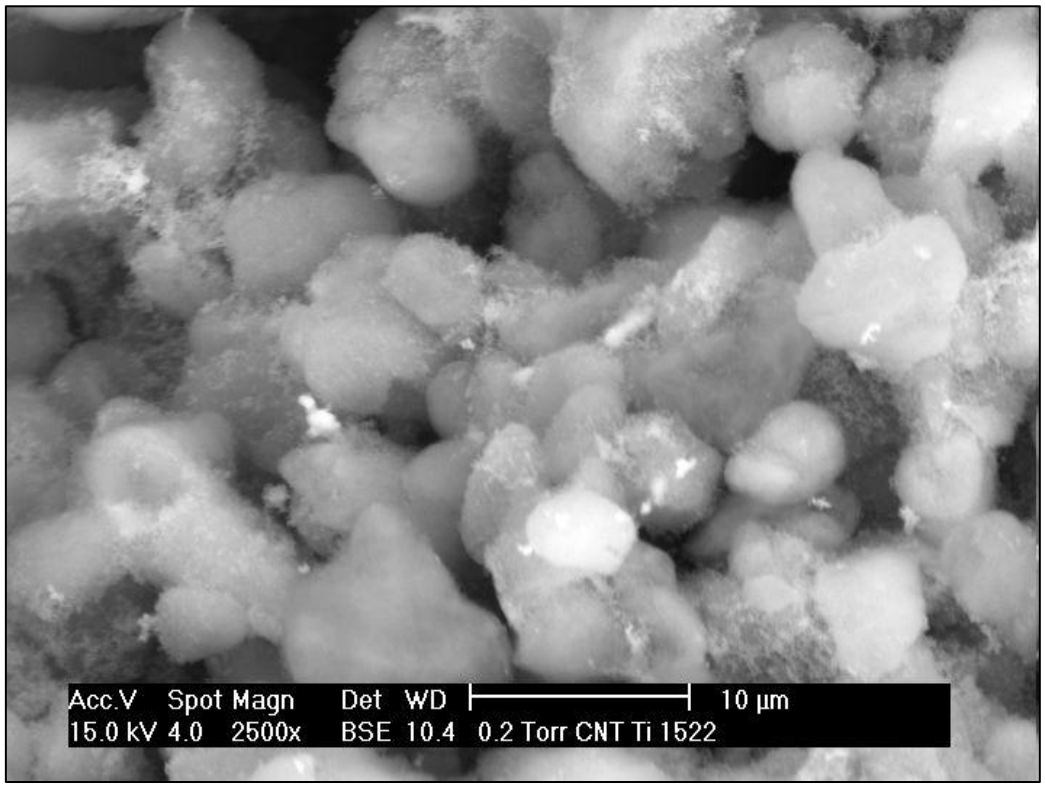
ESEM of Carbon Nanofibers with Al

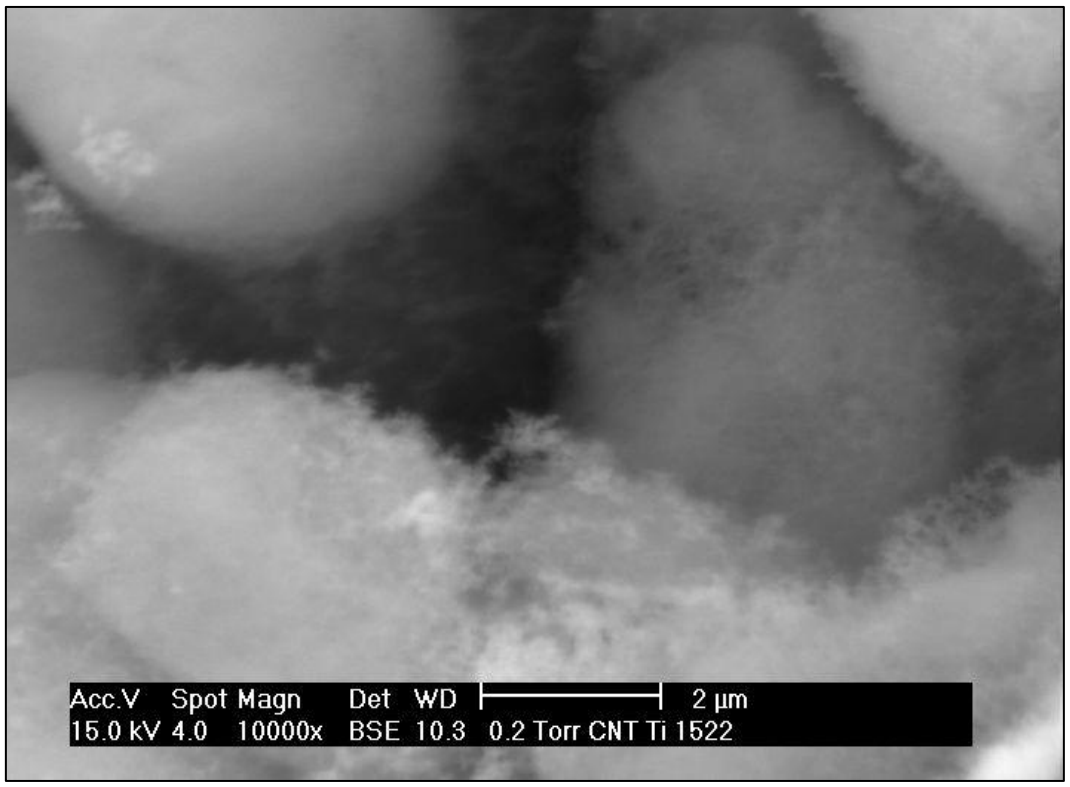


ESEM and EDX of Carbon nanotubes / carboxylic groups (CNT-COOH)



ESEM of Carbon nanotubes with Titanium





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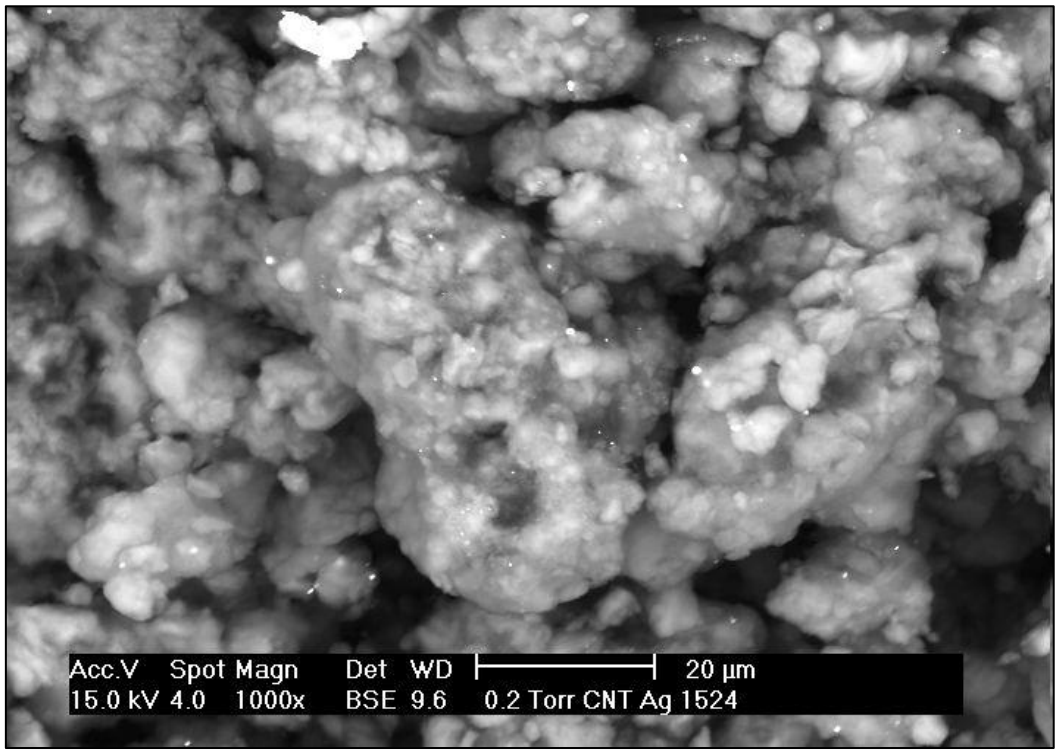
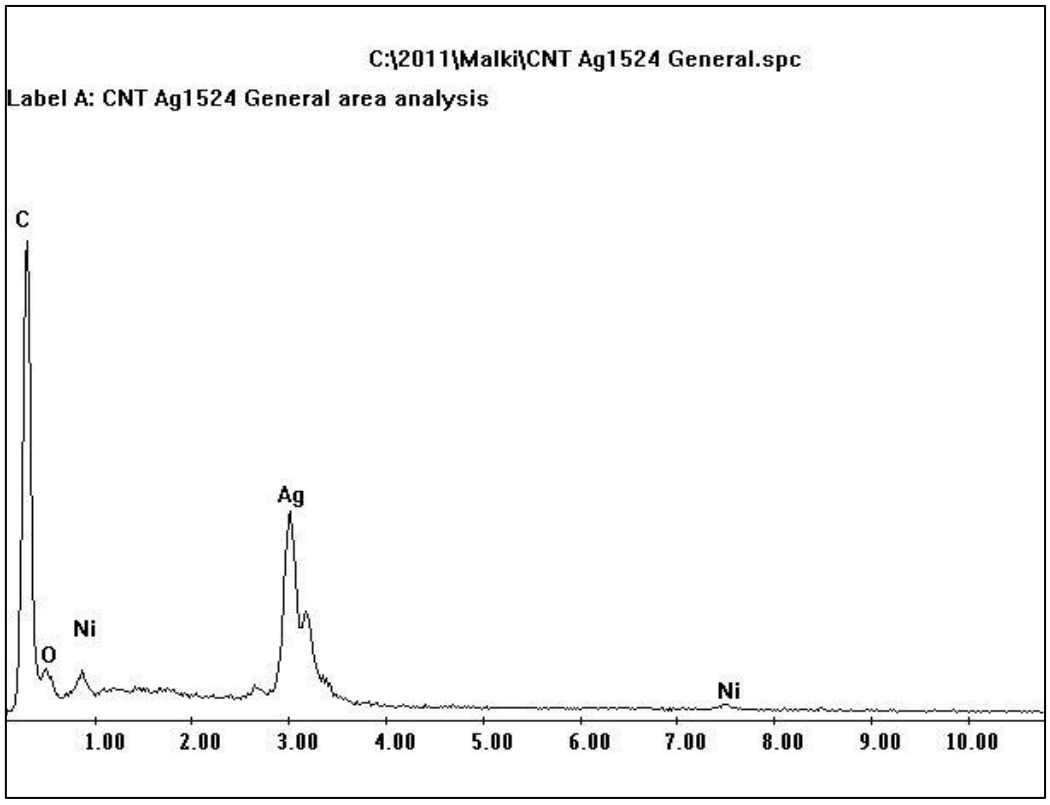
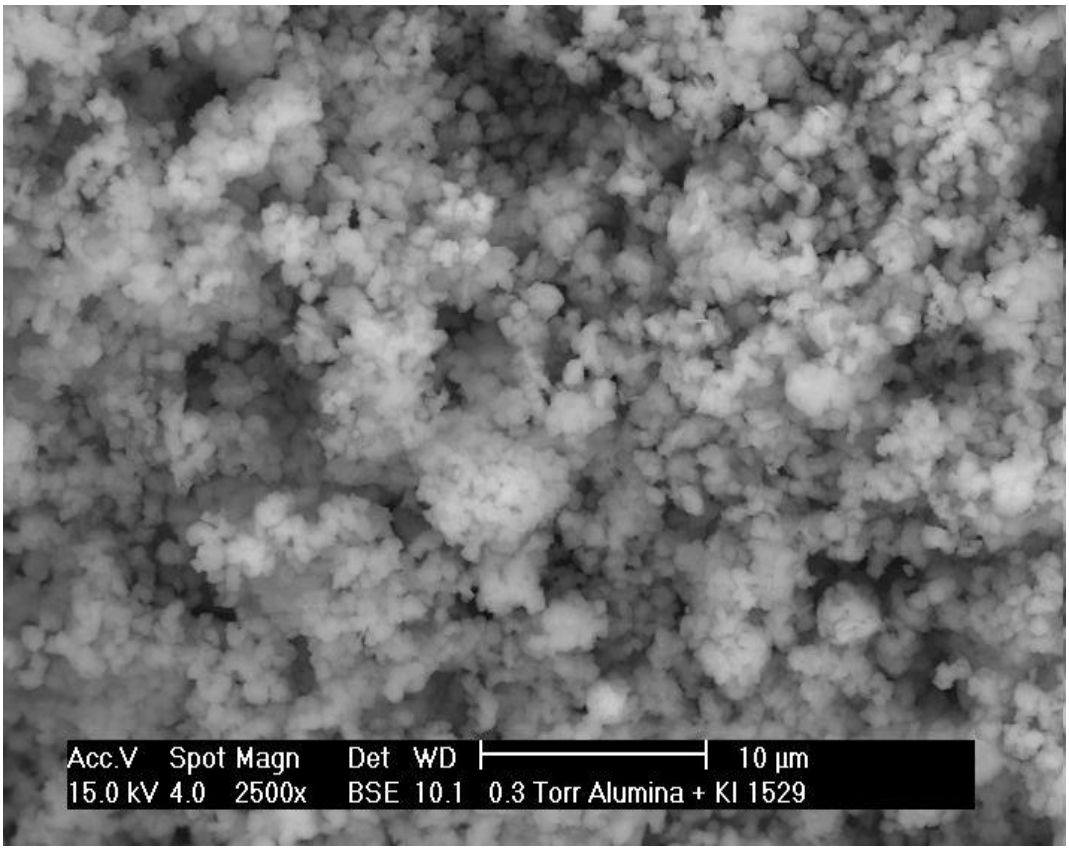
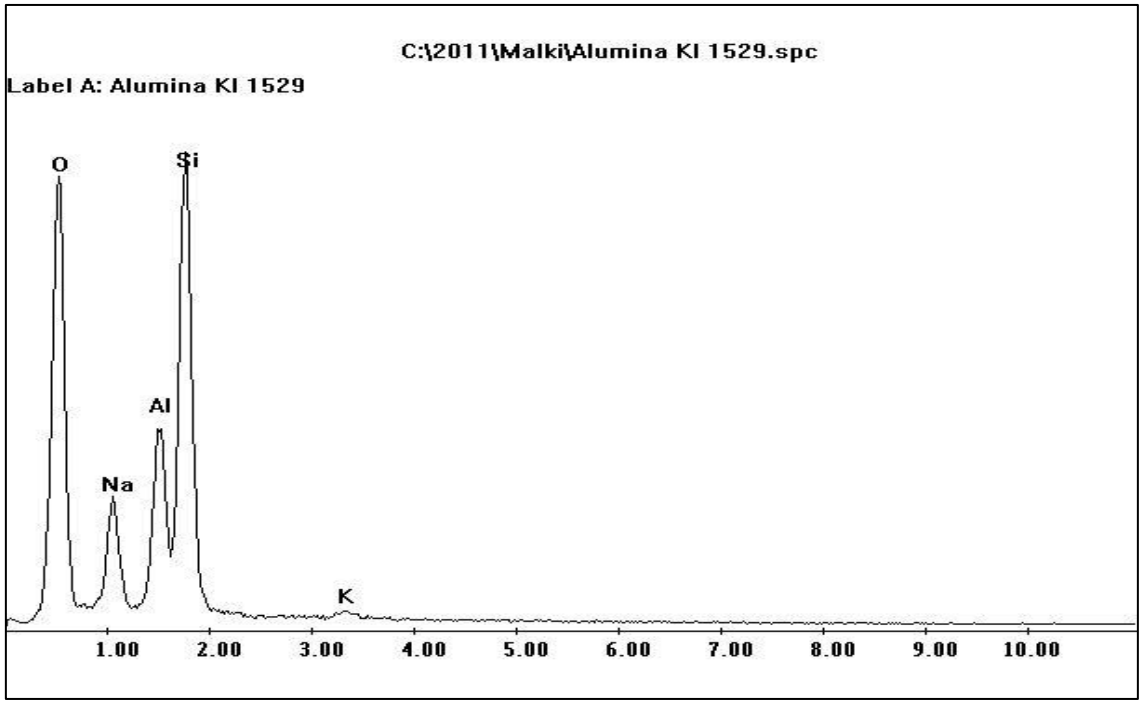


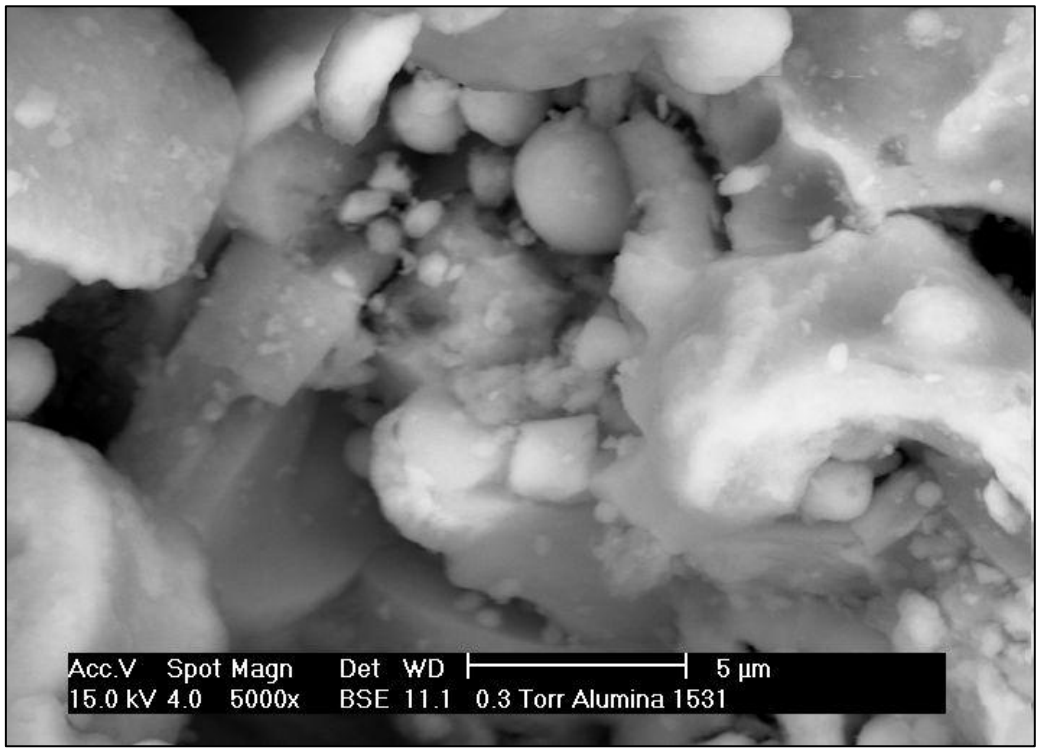


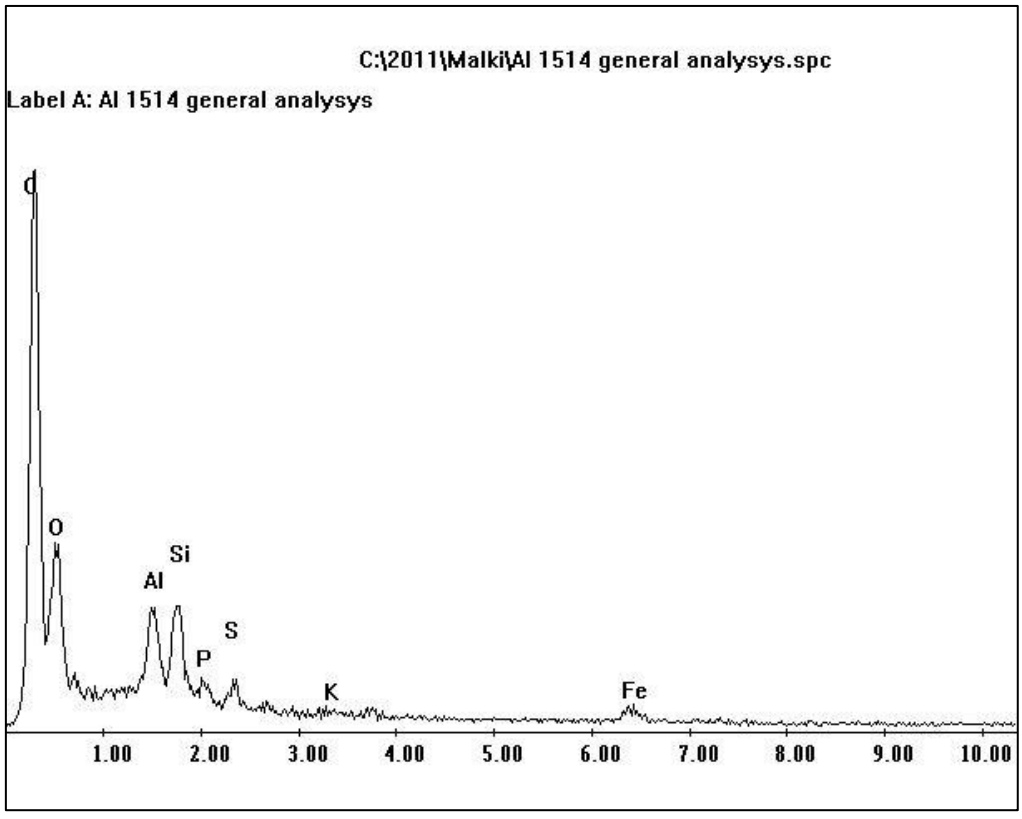
ESEM and EDX of Alumina with KI





ESEM and EDX of Alumina





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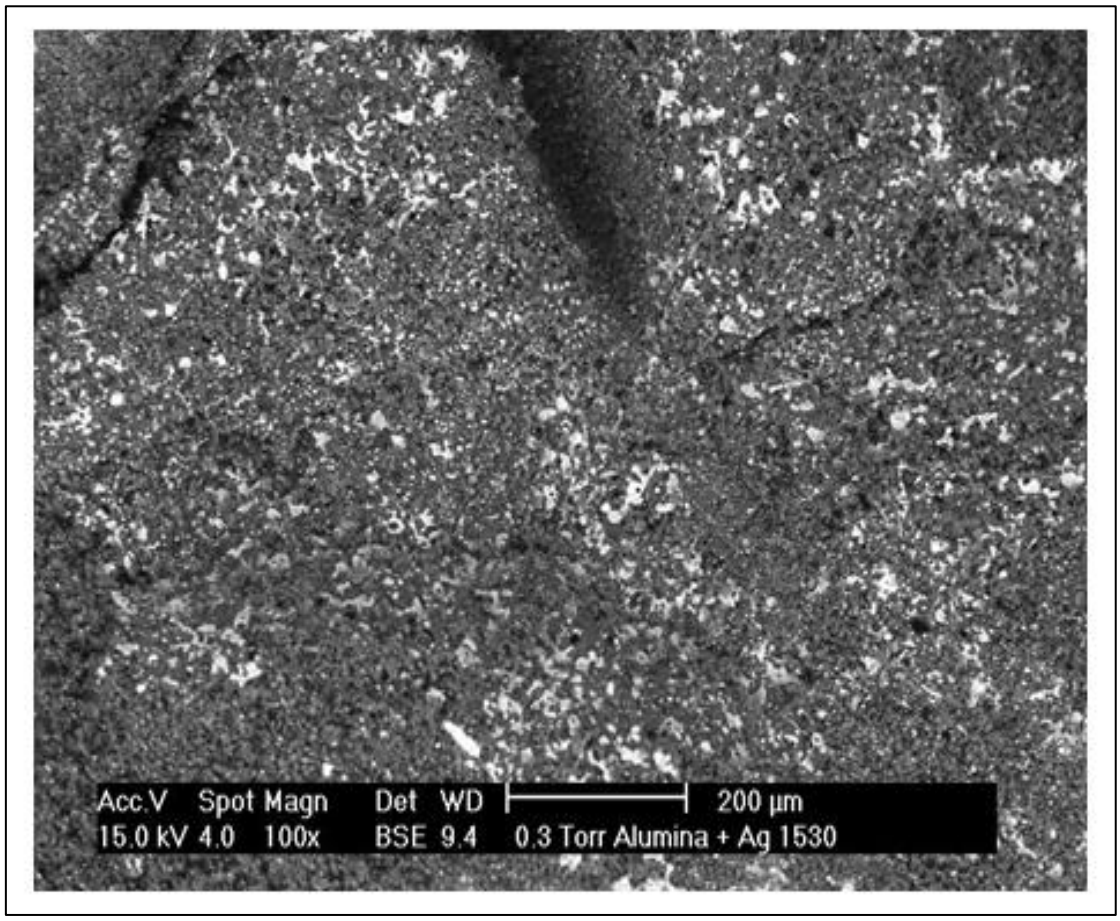
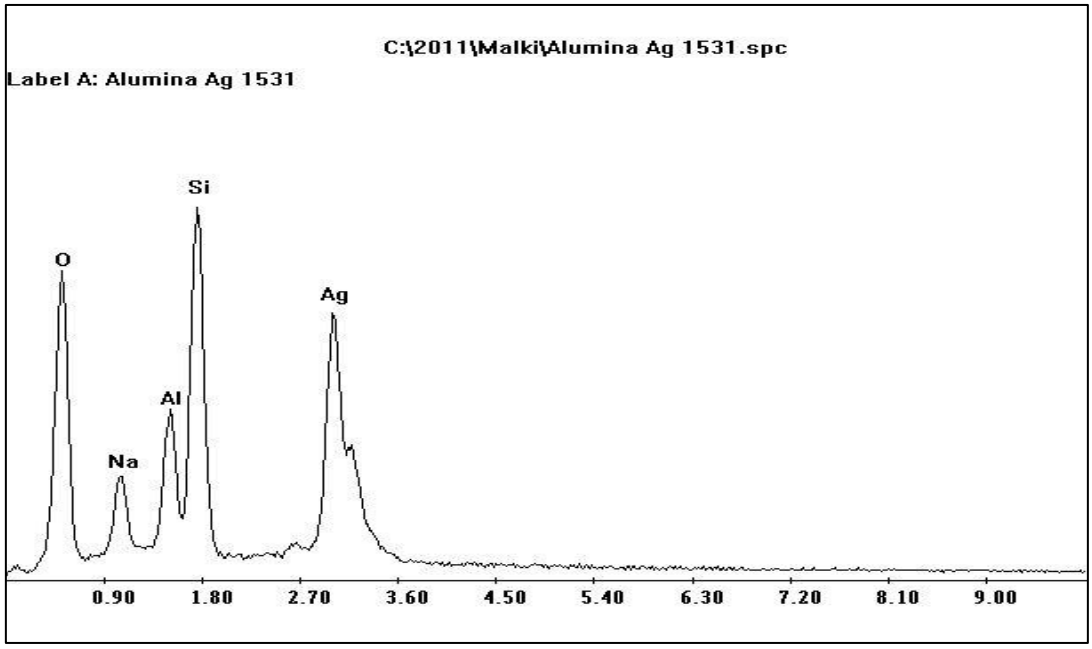
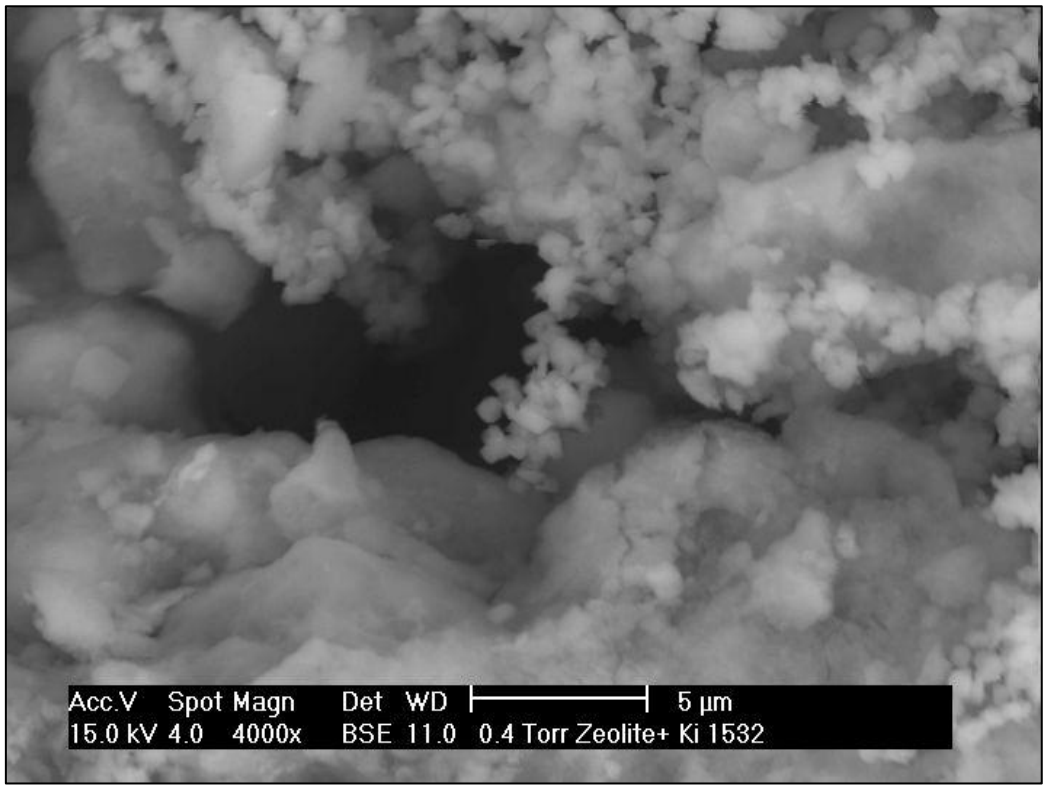




ESEM of Zeolite with KI



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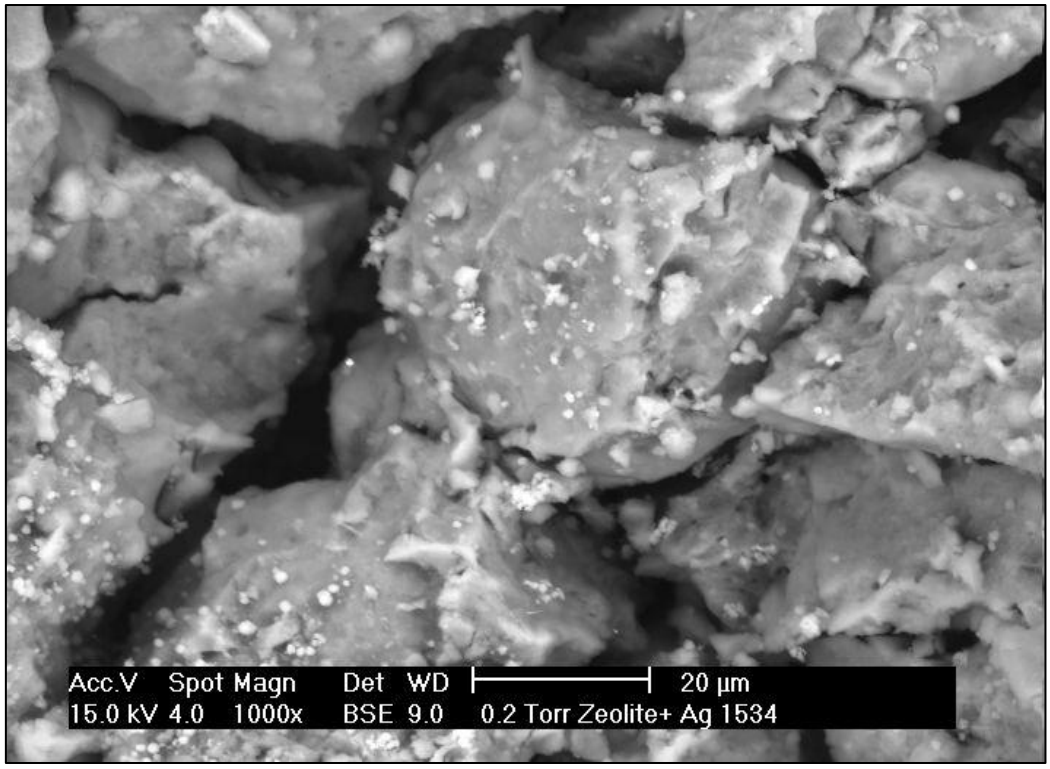
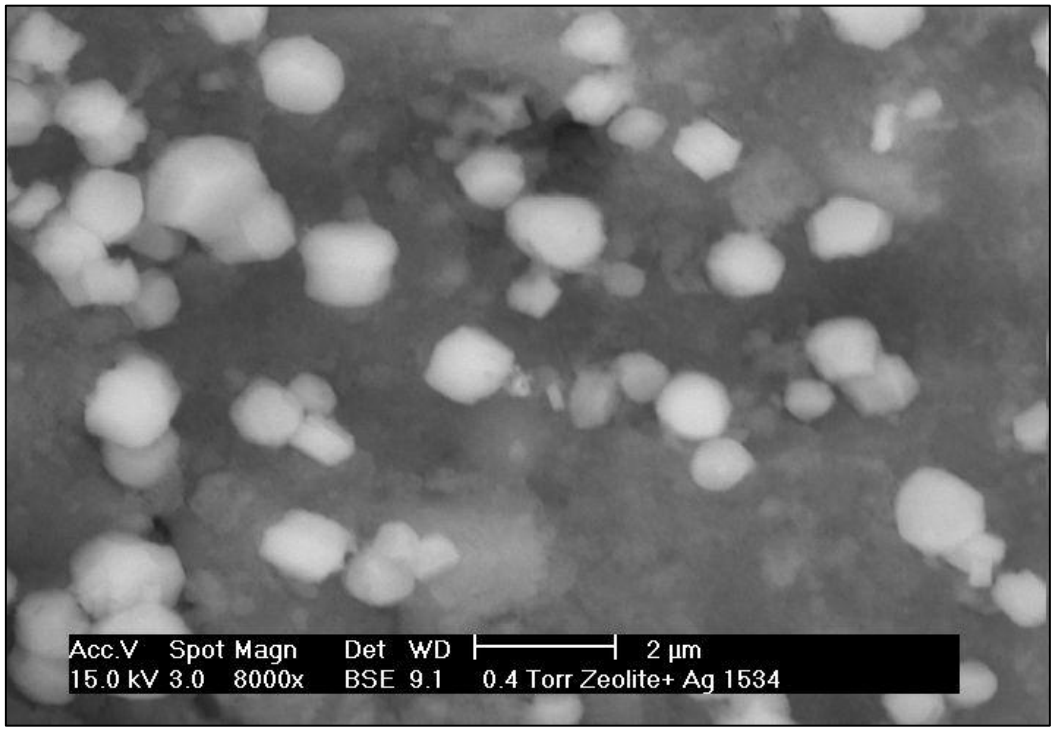
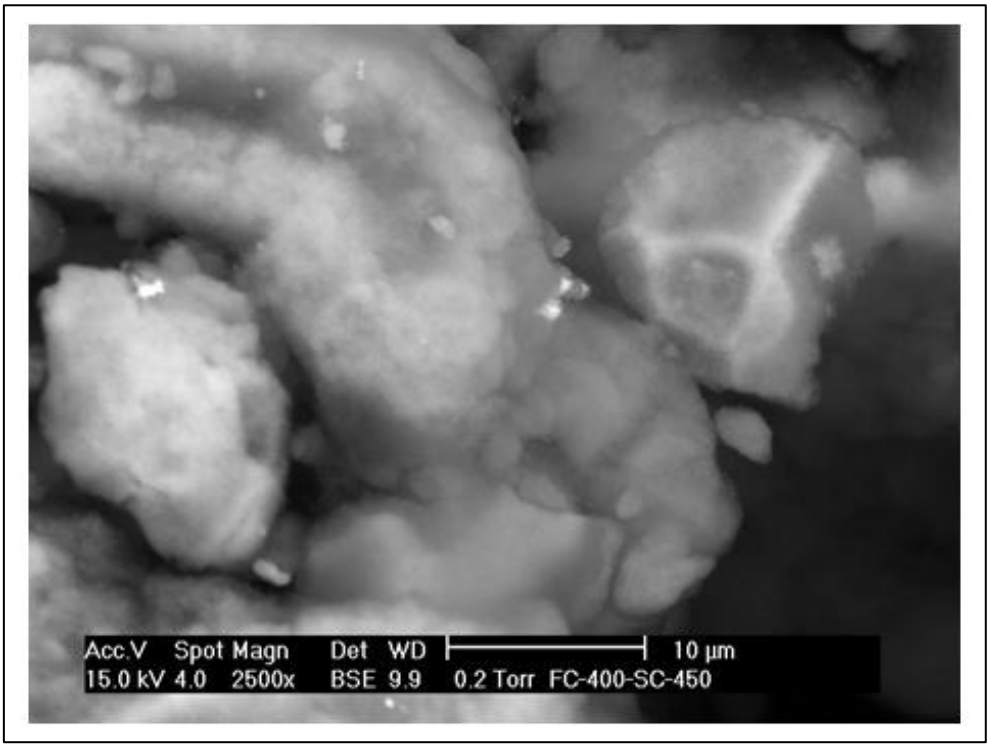
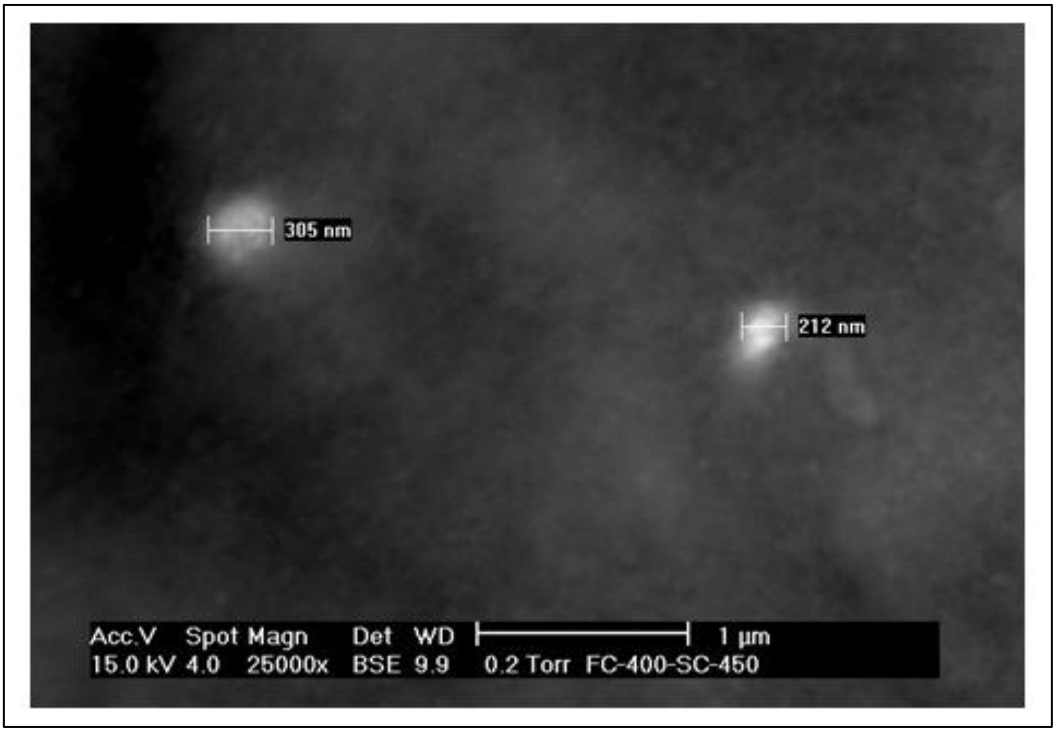


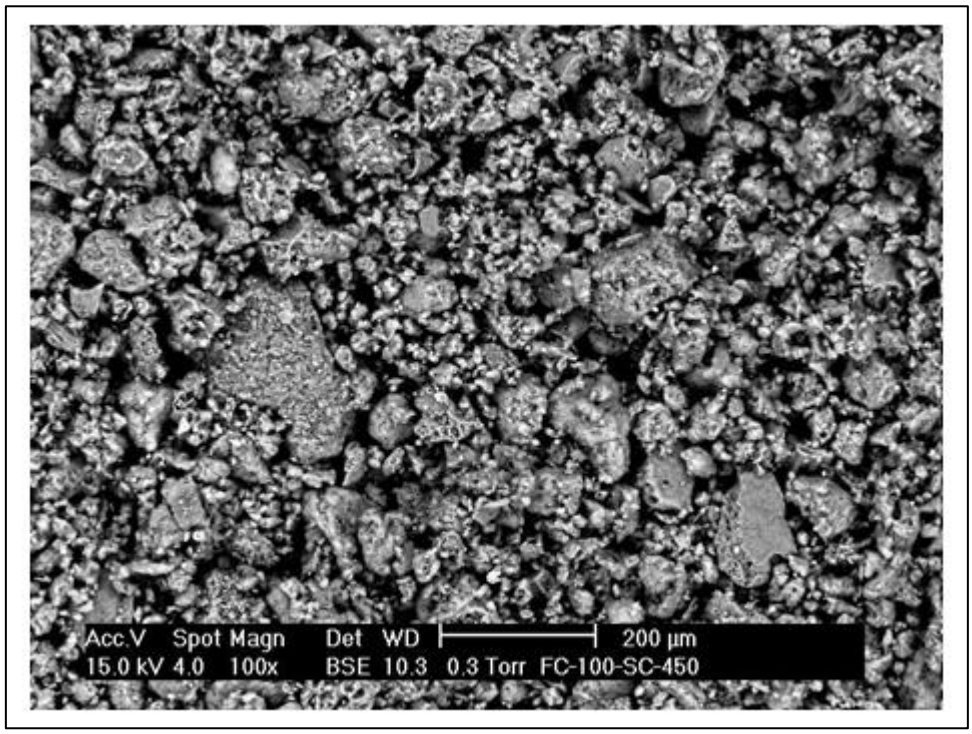


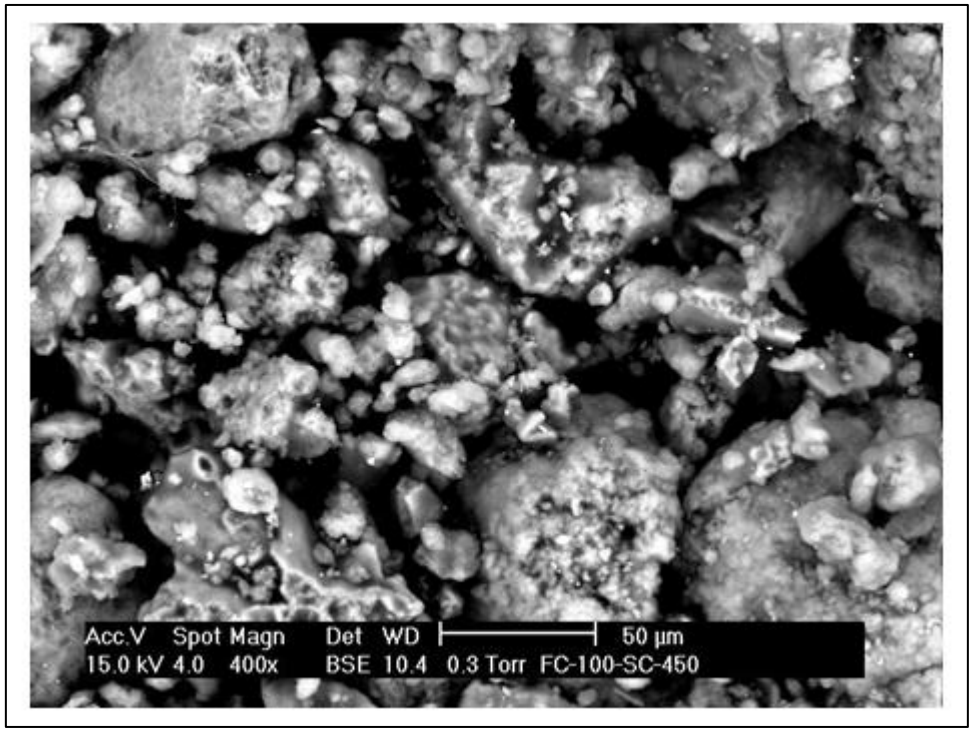
Carbon nanotube with Elemental Sulfur Prepared at 400 °C



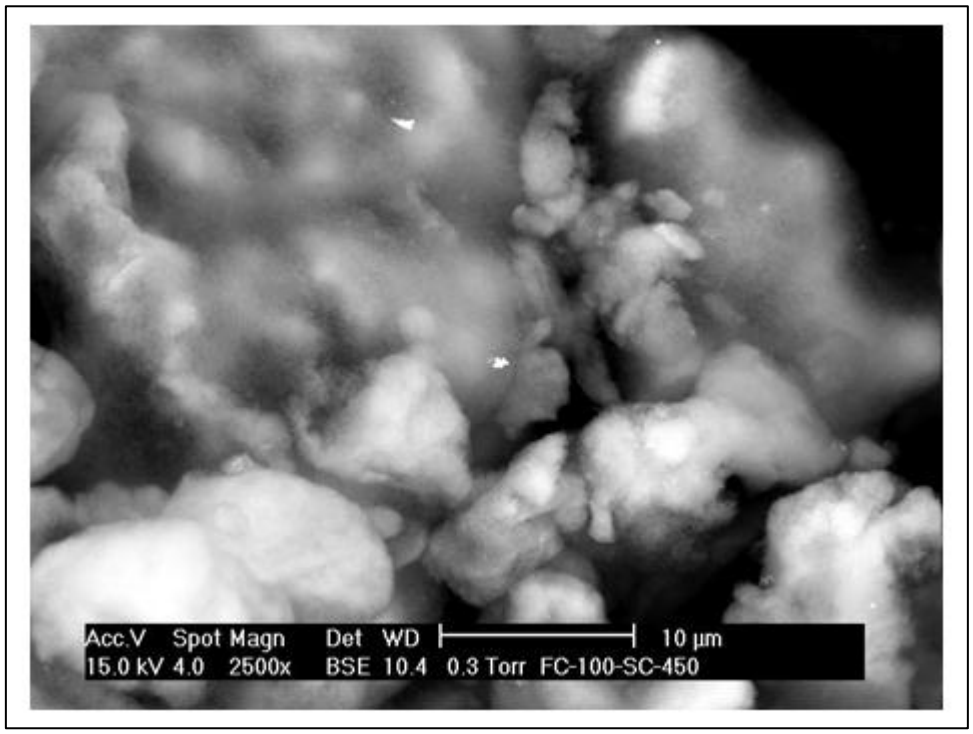


Carbon nanotube with Sulfur Prepared at 100 °C

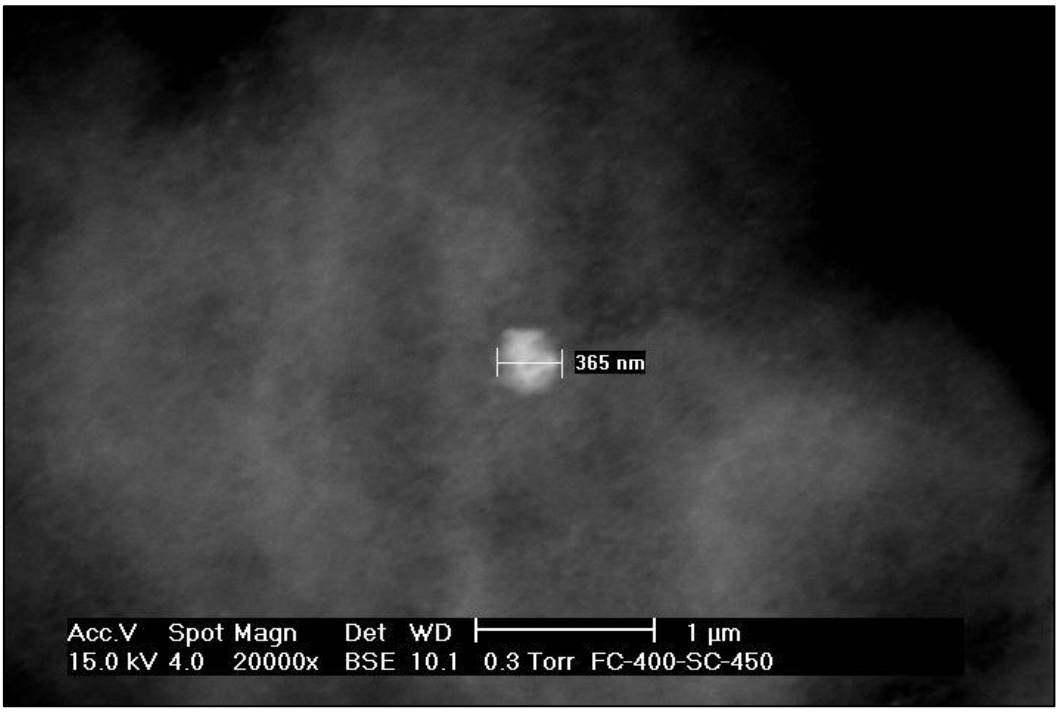




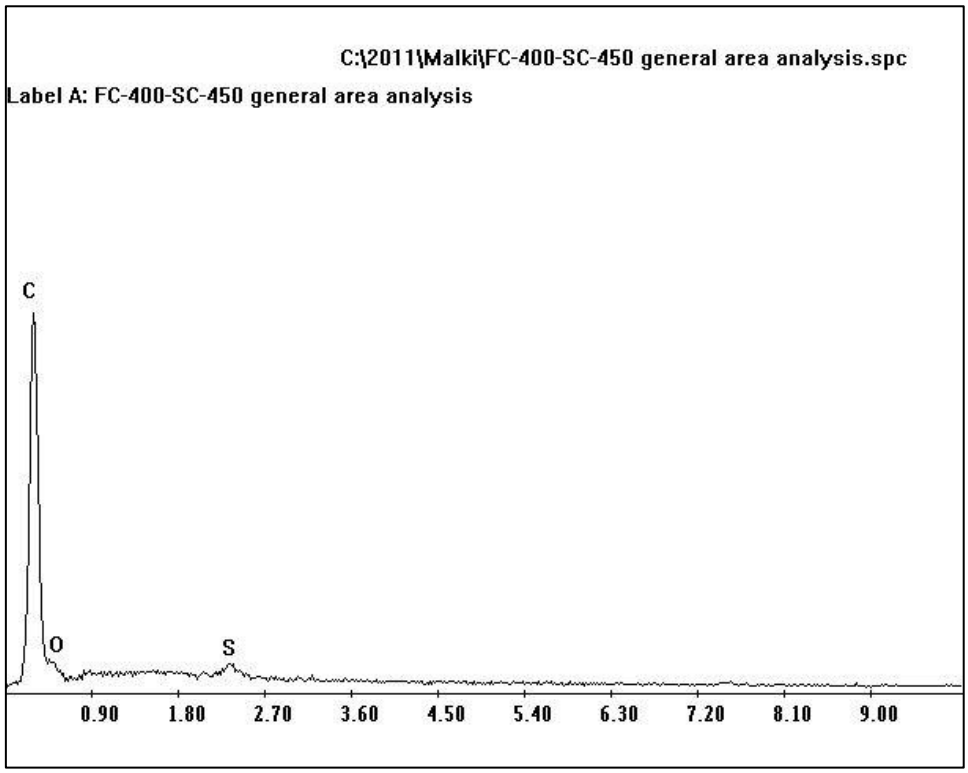
Carbon nanotube with Elemental Sulfur Prepared at 100 °C



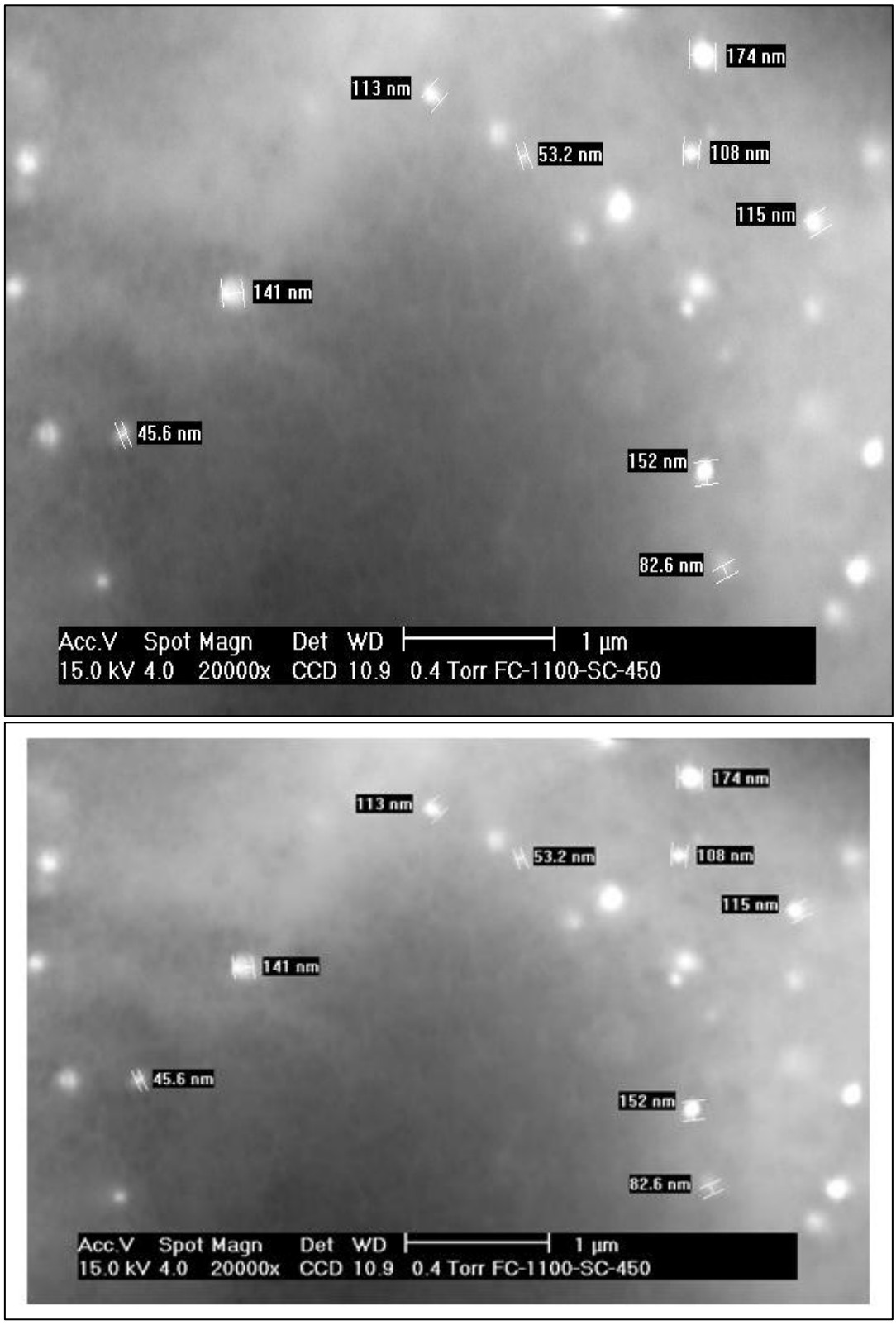
Carbon nanotube with Sulfur Prepared at 400 °C



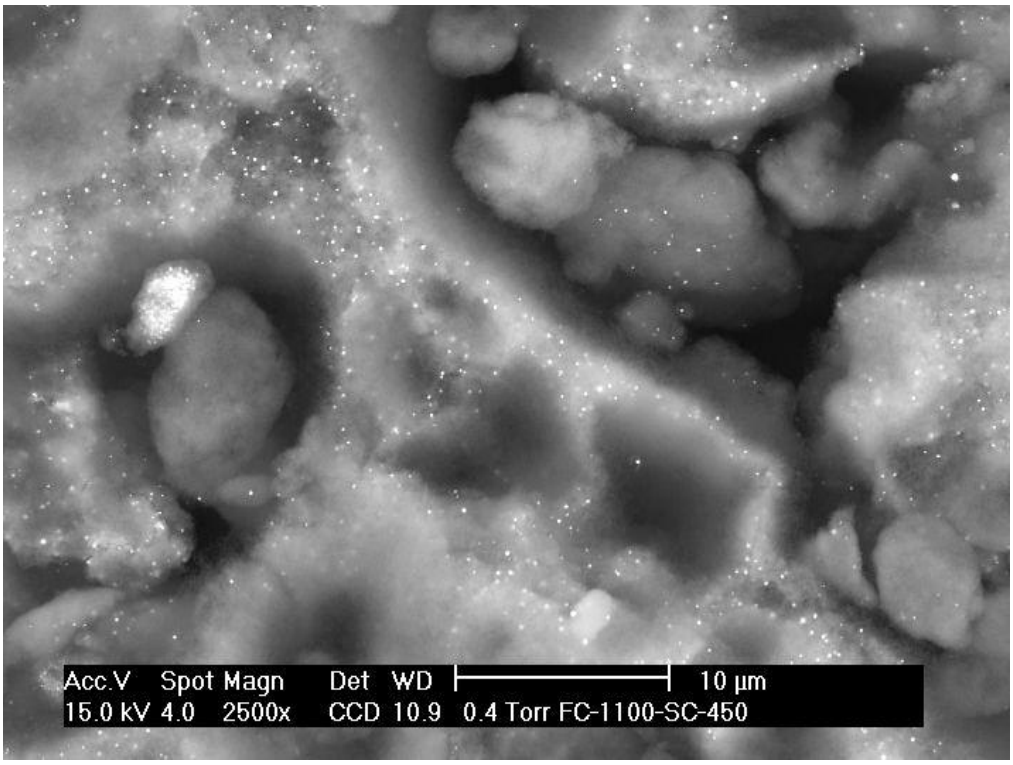
EDX of Carbon Nanotube with Elemental Sulfur Prepared at 100 °C

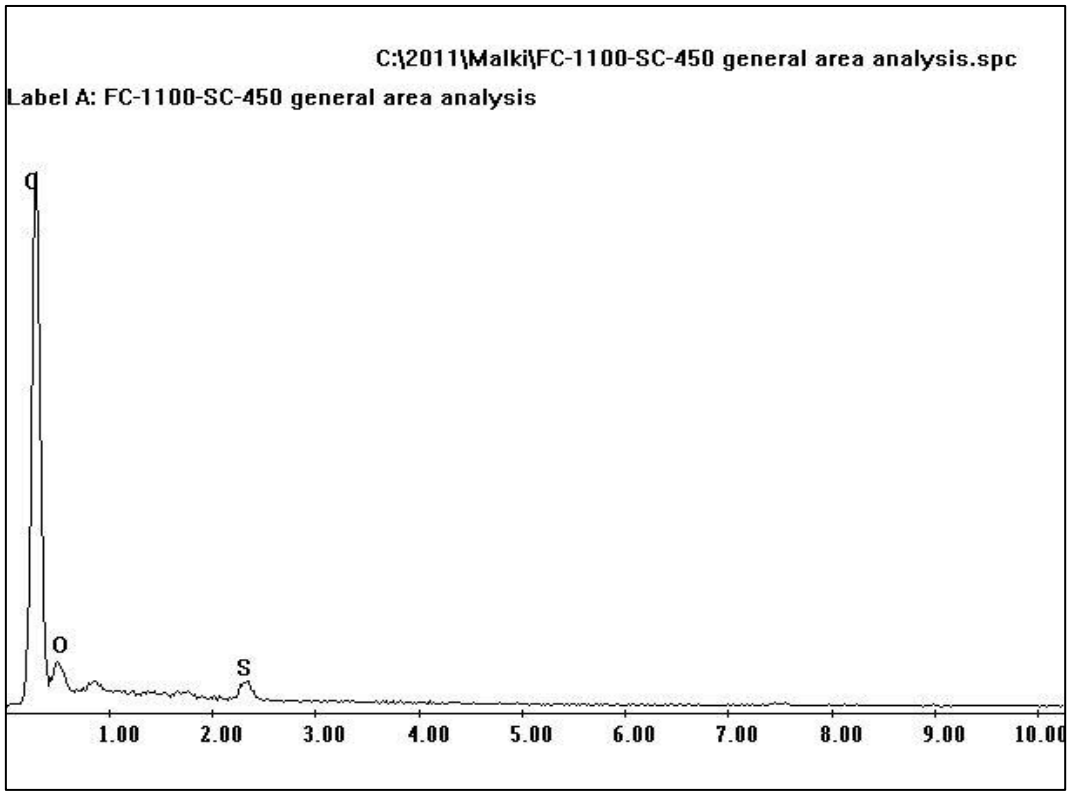


ESEM of Carbon nanotube with Sulfur Prepared at 1100 °C

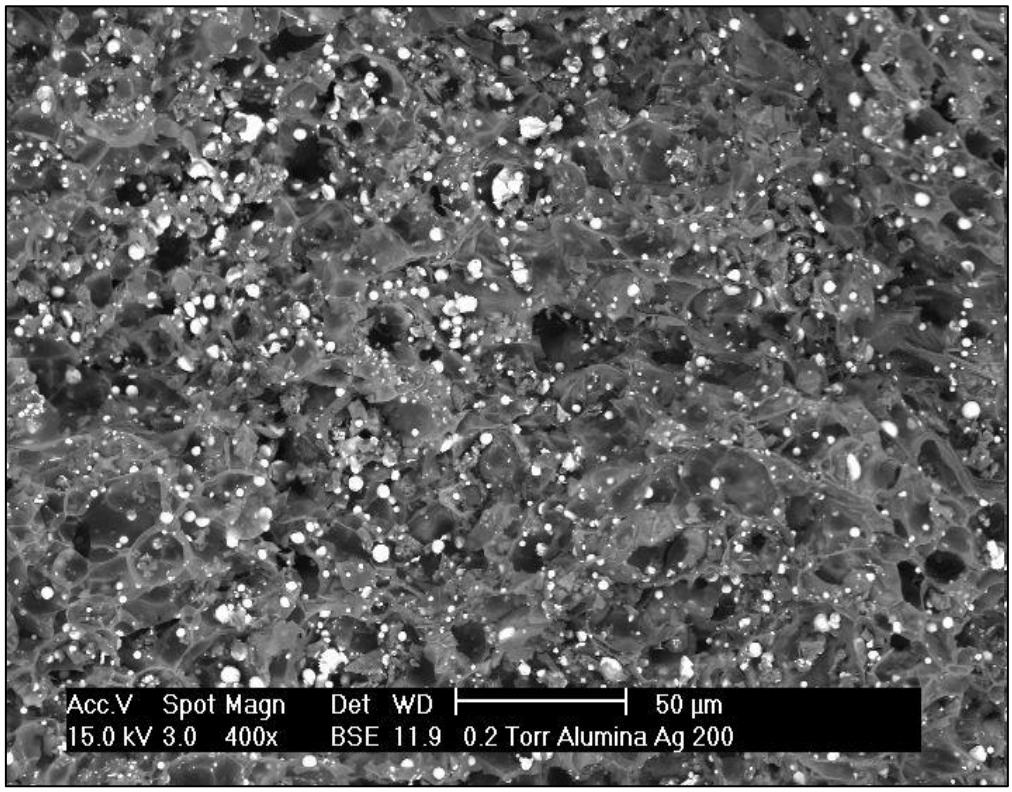


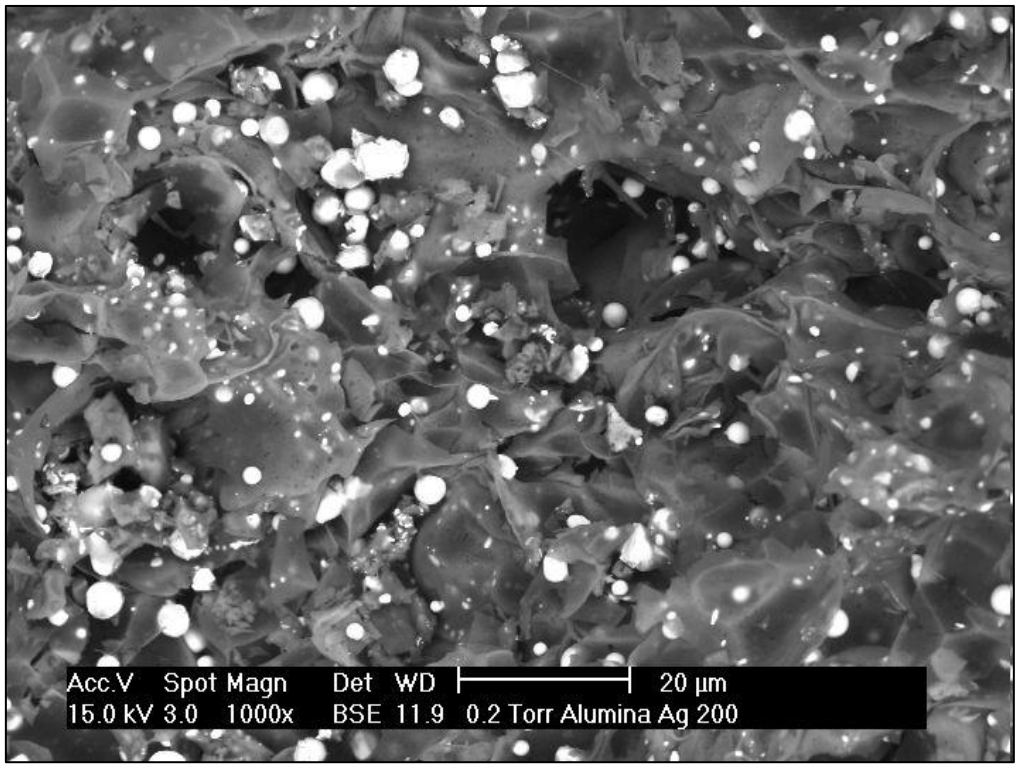
ESEM and EDX of Carbon nanotube with Sulfur Prepared at 1100 °C





ESEM of Alumina with Ag





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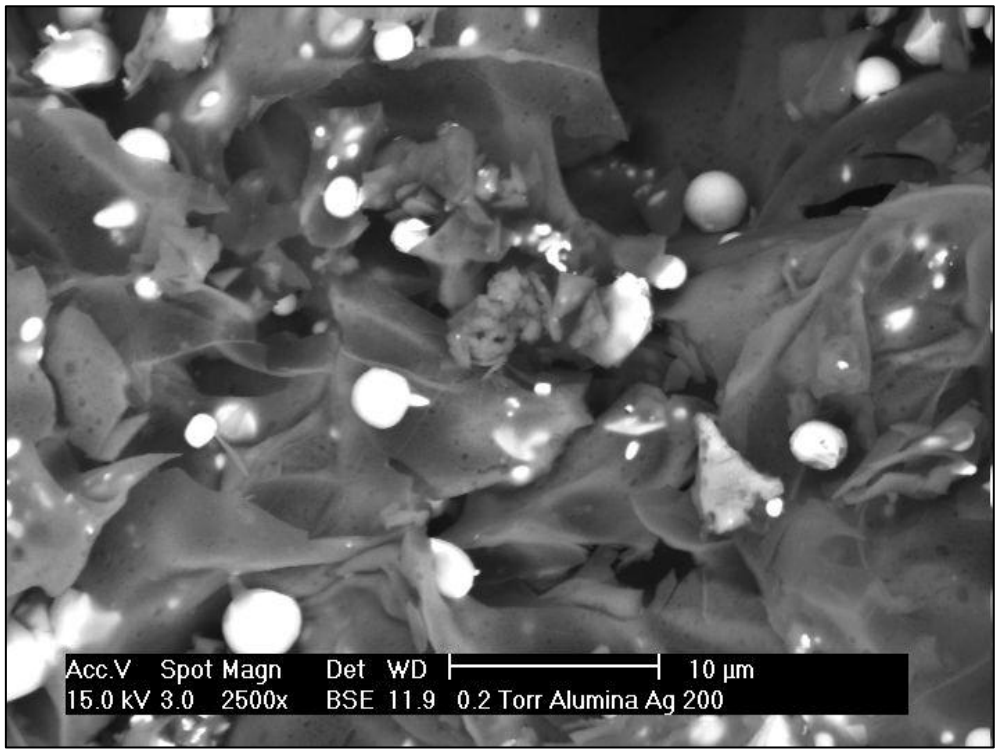
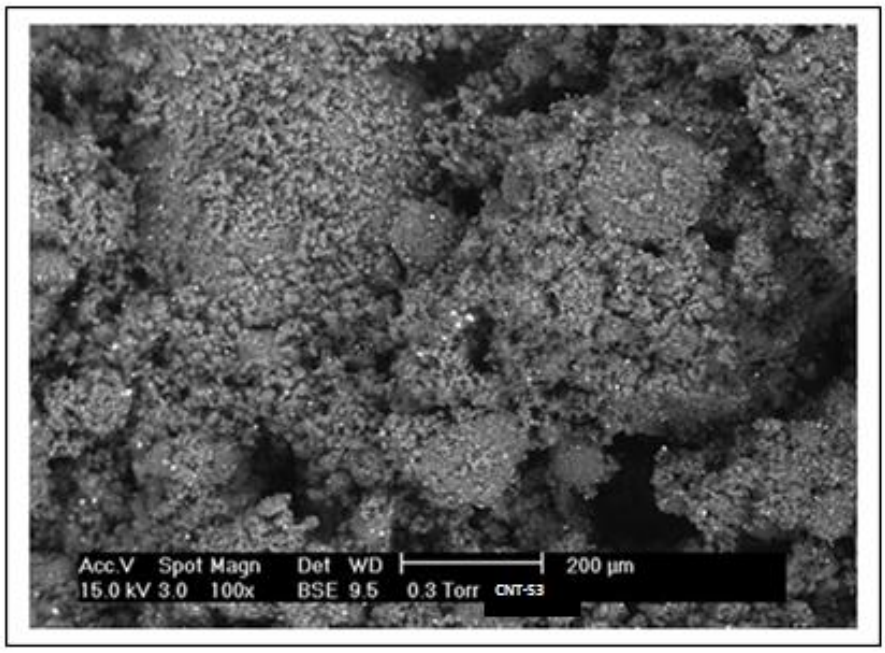
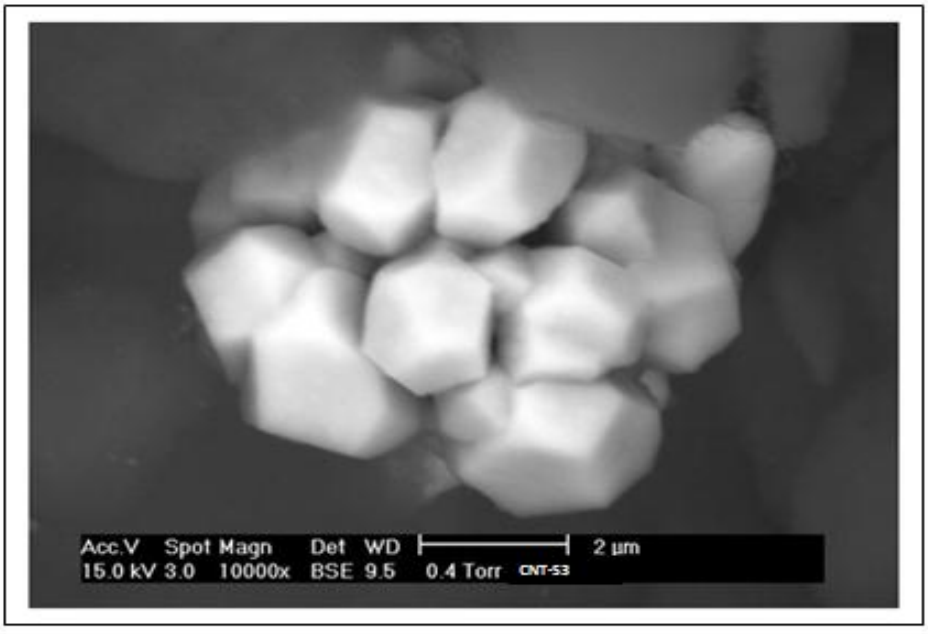
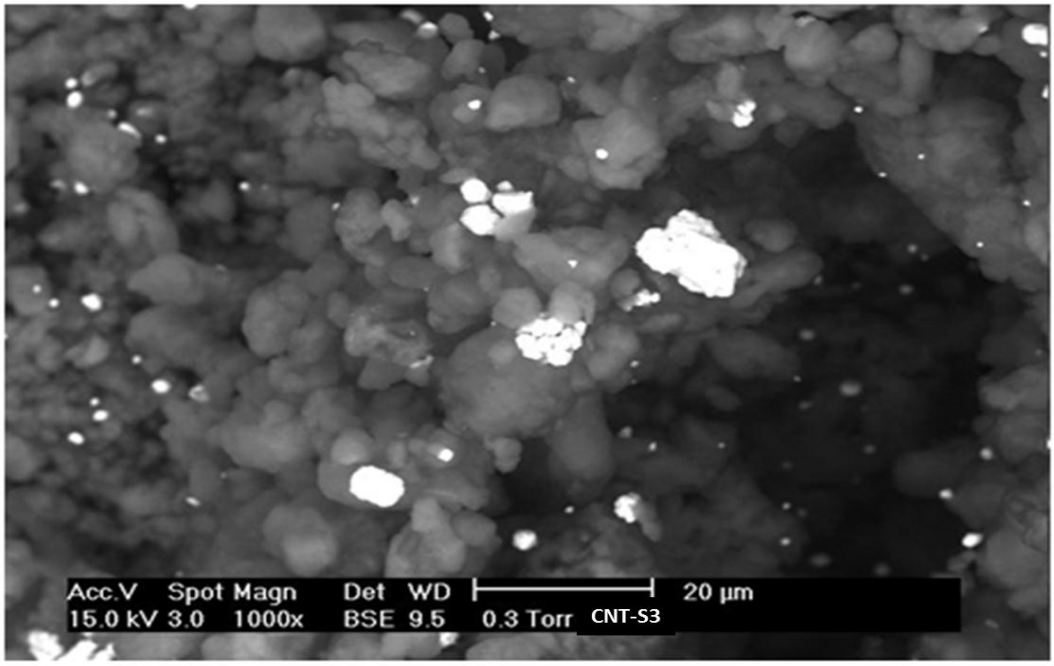


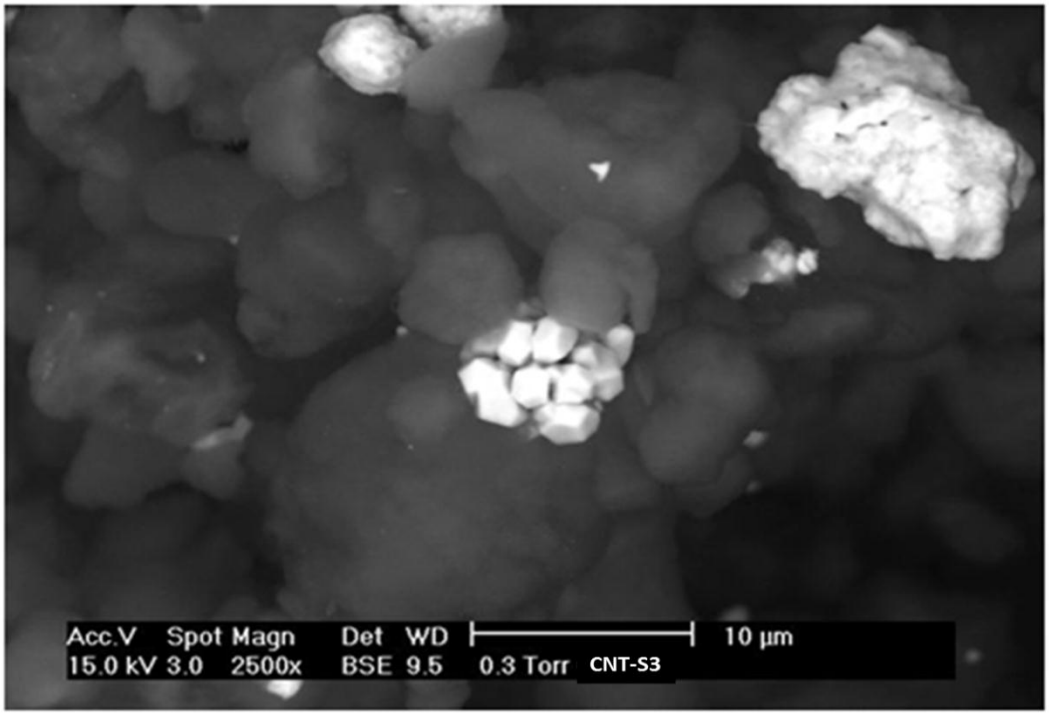
Carbon nanotube with Elemental Sulfur prepared 700 °C (CNT-S3)



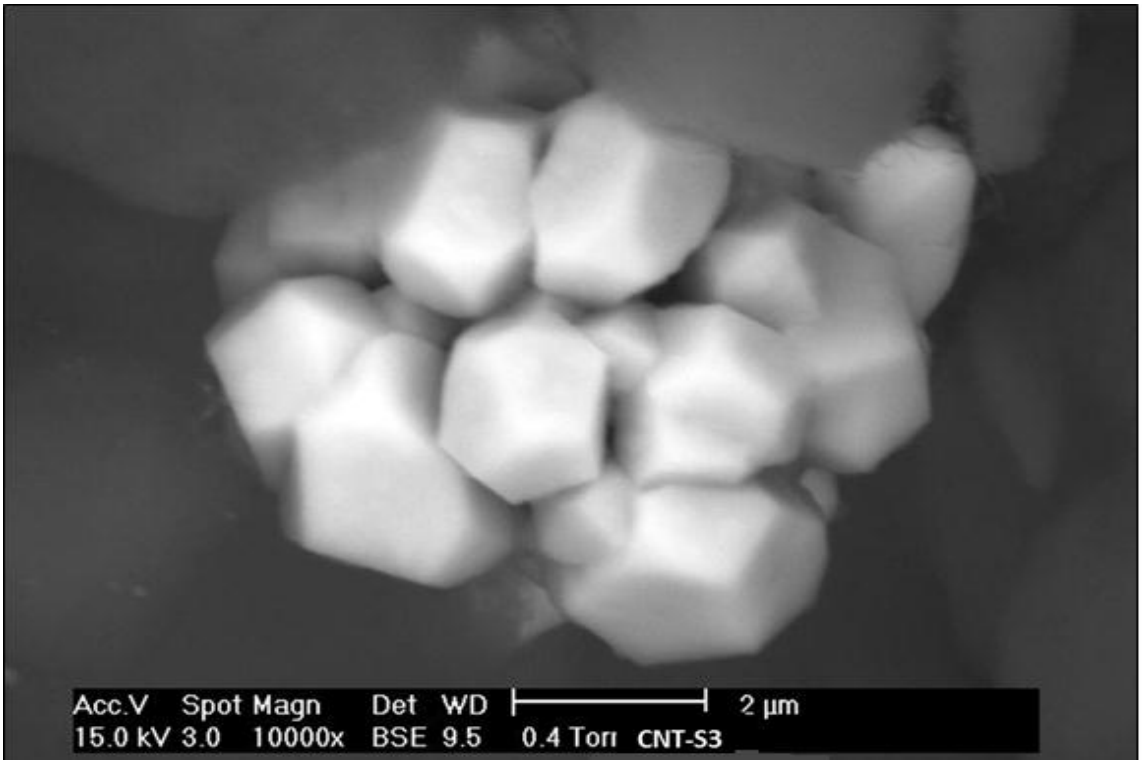


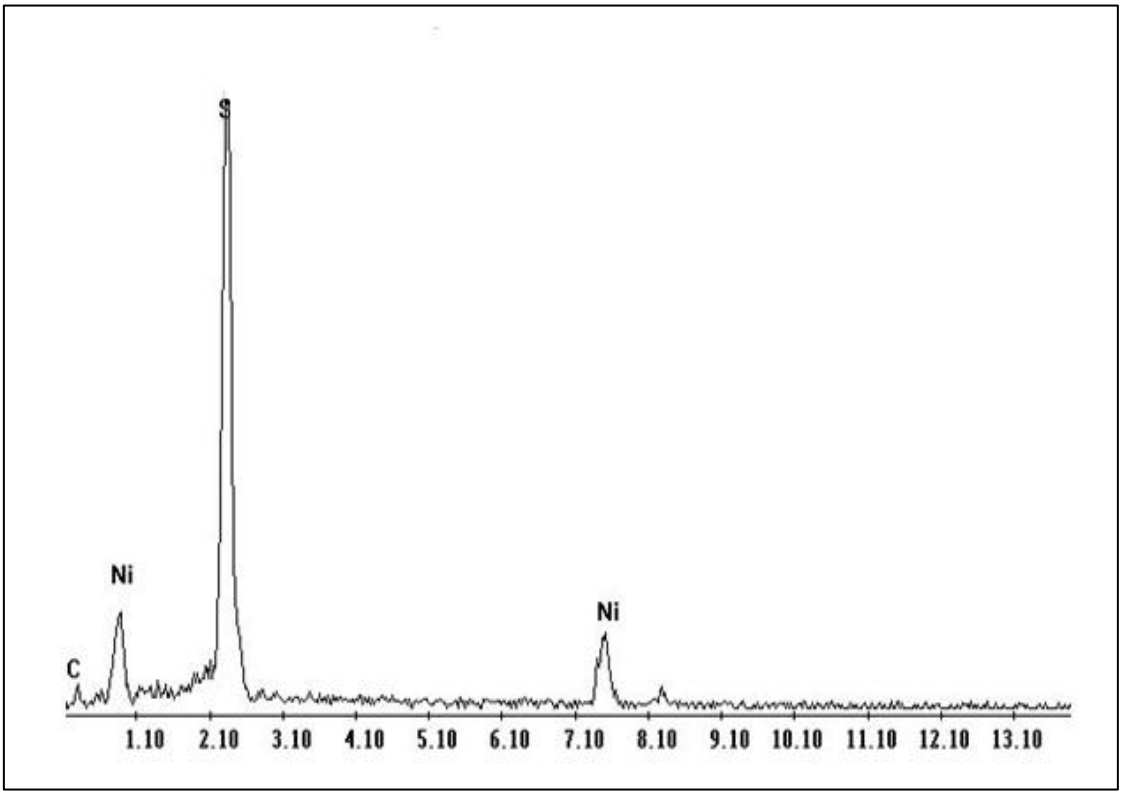
Carbon nanotube with Sulfur prepared at 700 °C





ESEM and EDX of Carbon Nanotube with Elemental Sulfur (CNTS3) prepared at 700 °C and 3 hrs

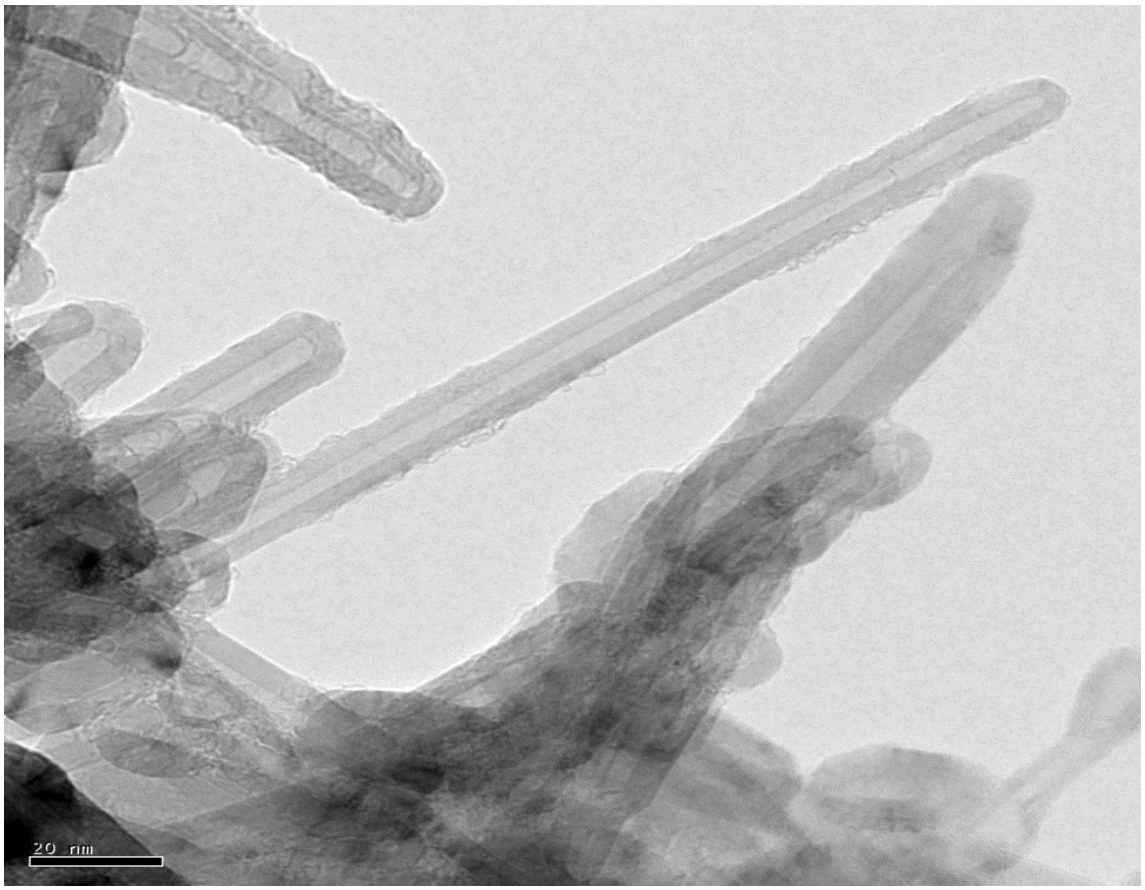


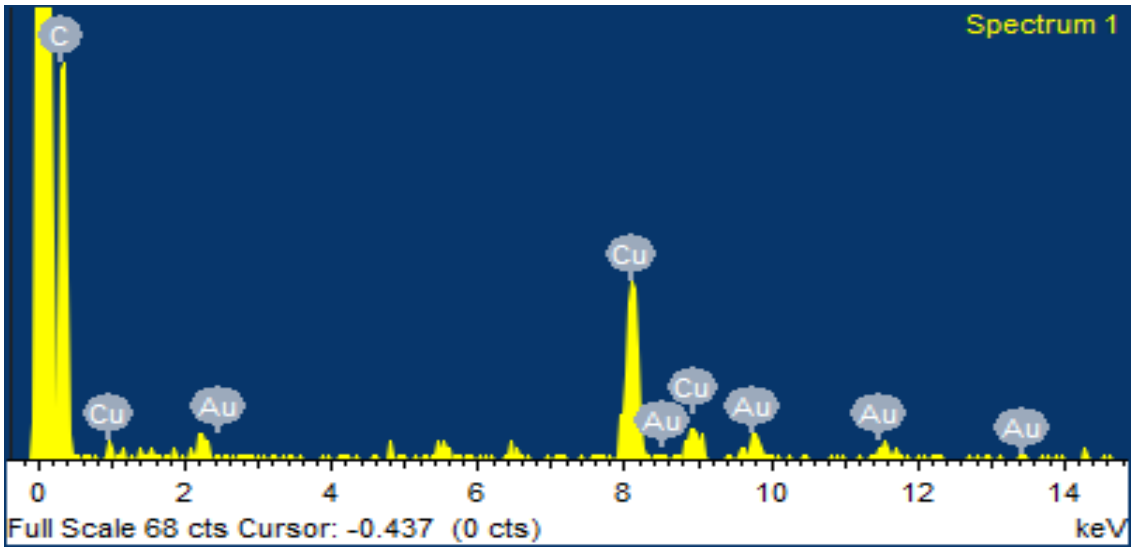


APPENDIX II

TEM and EDX for CNFs and CNTs With Fe and Ti

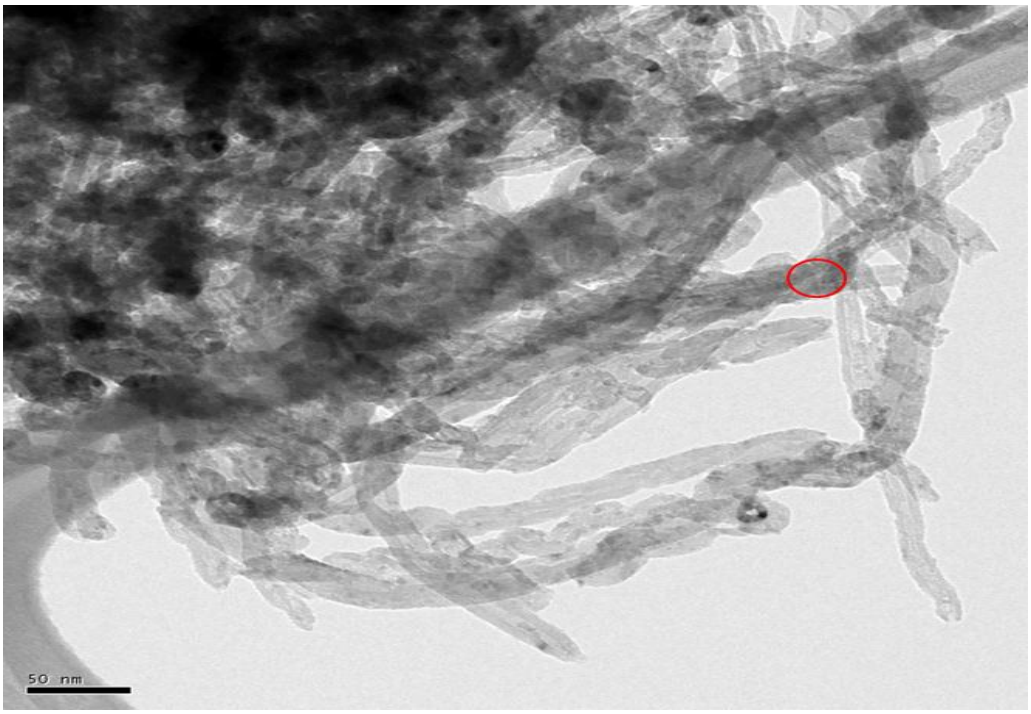
TEM and EDX of CNT

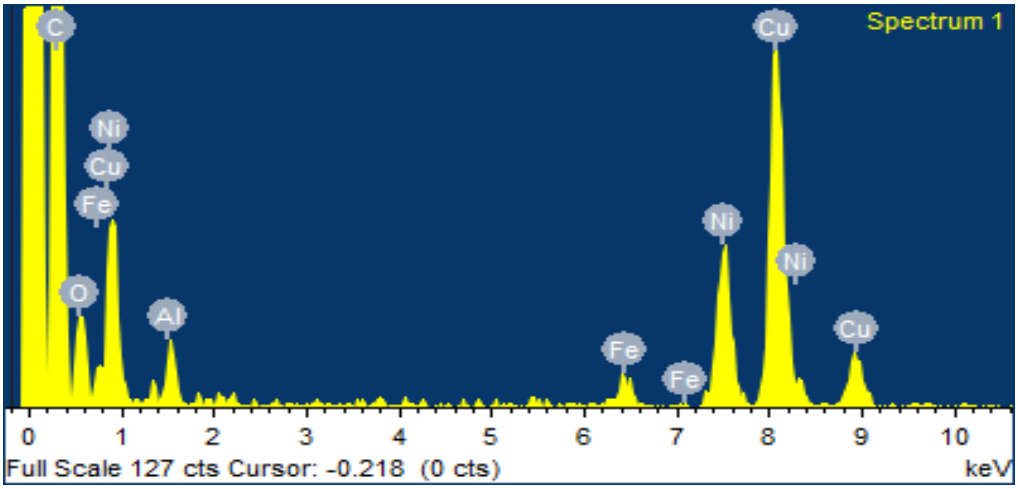




Element	Weight%	Atomic%	
C K	93.38	99.57	
Au L	6.62	0.43	
Totals	100.00		

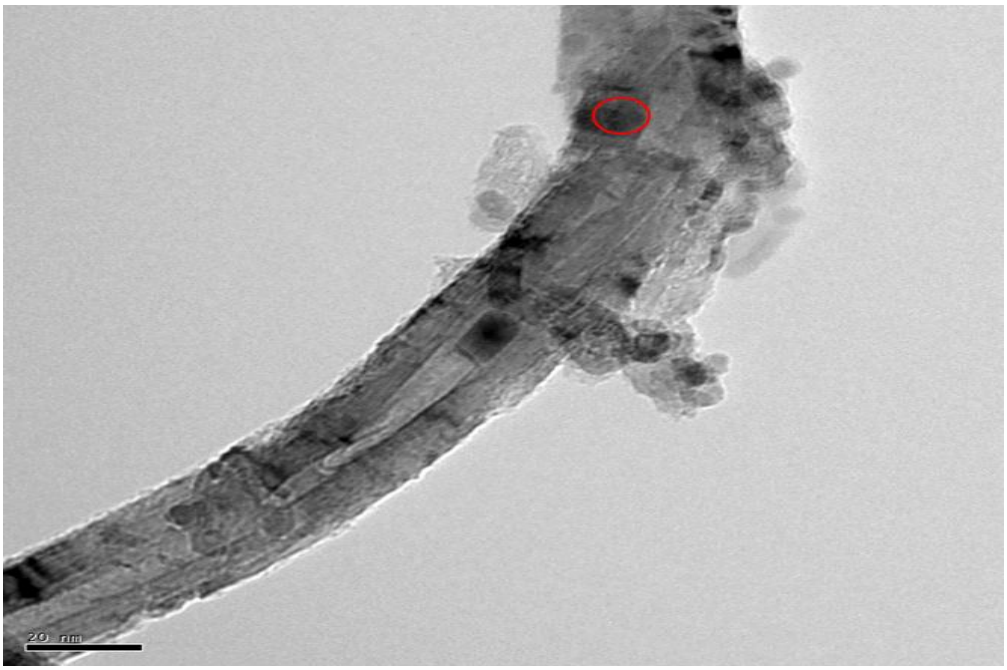
TEM and EDX of CNT-Fe

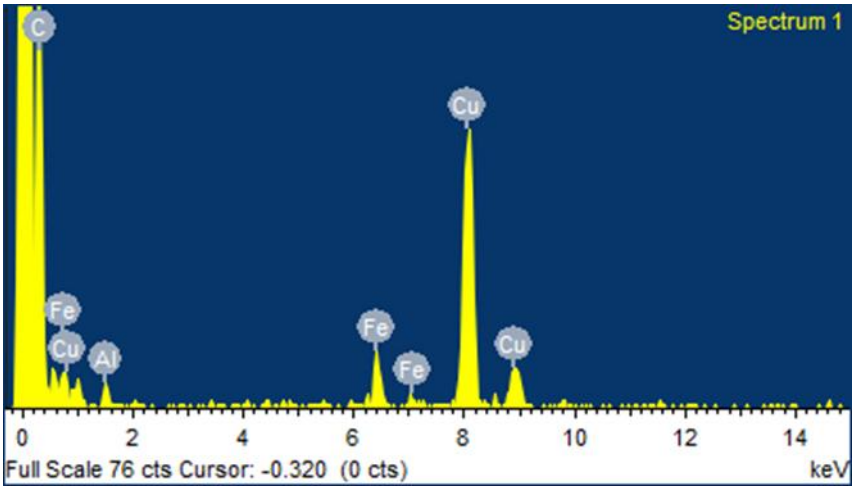




Element	Weight%	Atomic%	
C	81.16	92.05	
O	4.86	4.14	
Al	2.01	1.02	
Fe K	1.60	0.39	
Ni K	10.37	2.41	
Totals	100.00		

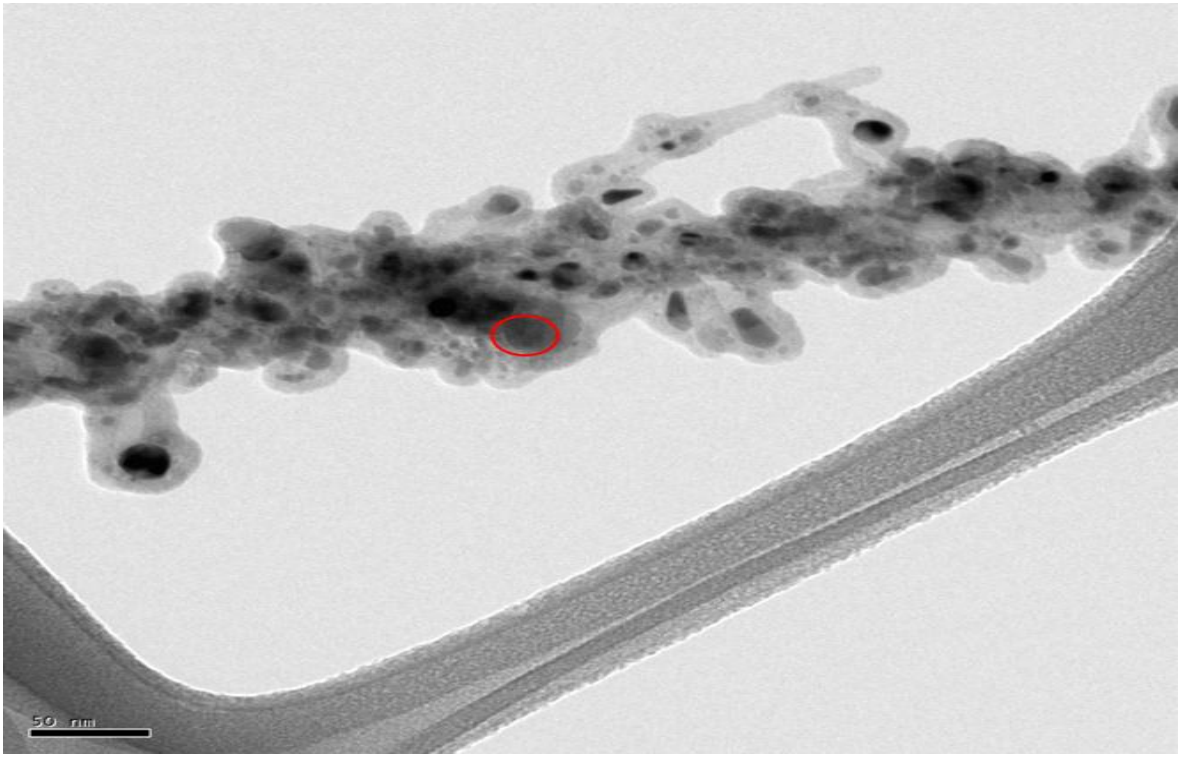
TEM and EDX of CNT-Fe

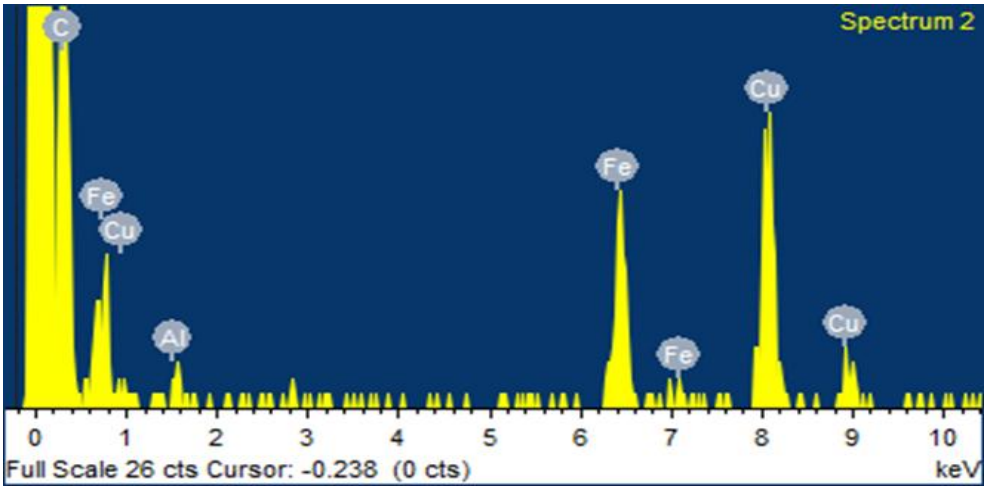




Element	Weight%	Atomic%	
C K	88.29	96.54	
Al K	2.80	1.37	
Fe K	8.91	2.10	
Totals	100.00		

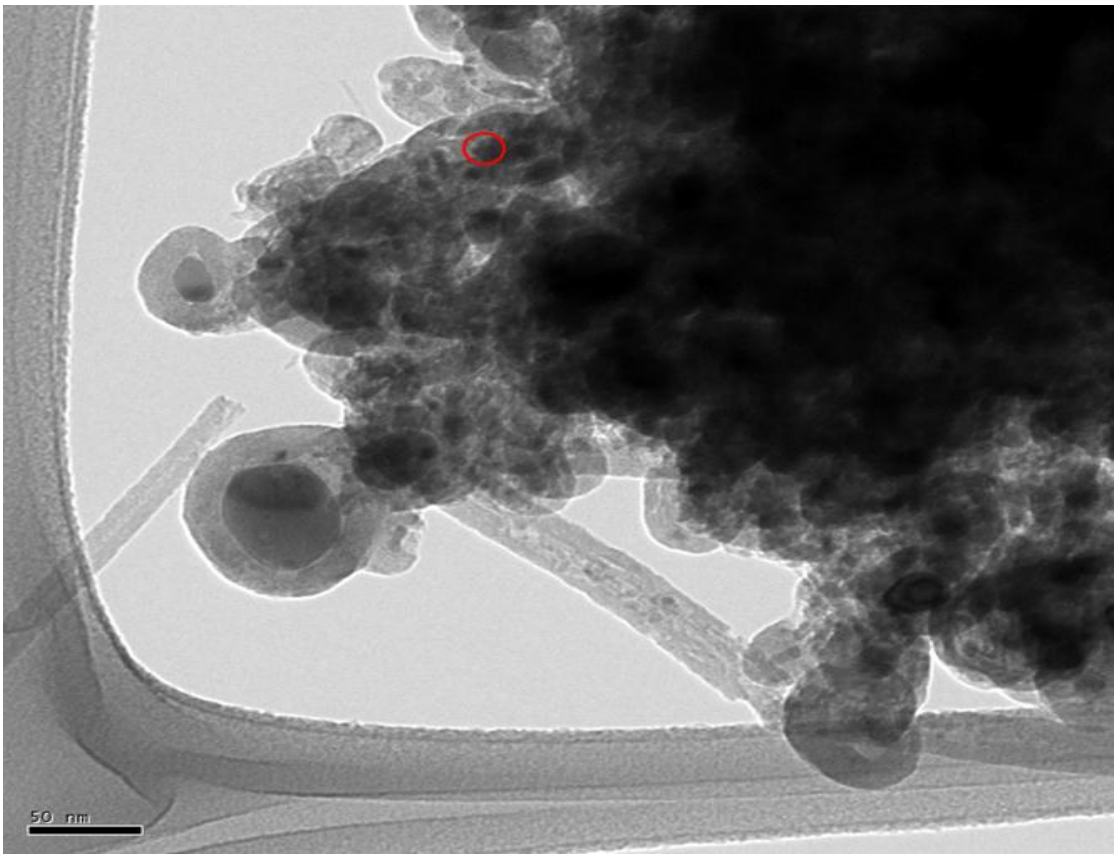
TEM and EDX of CNF-Fe

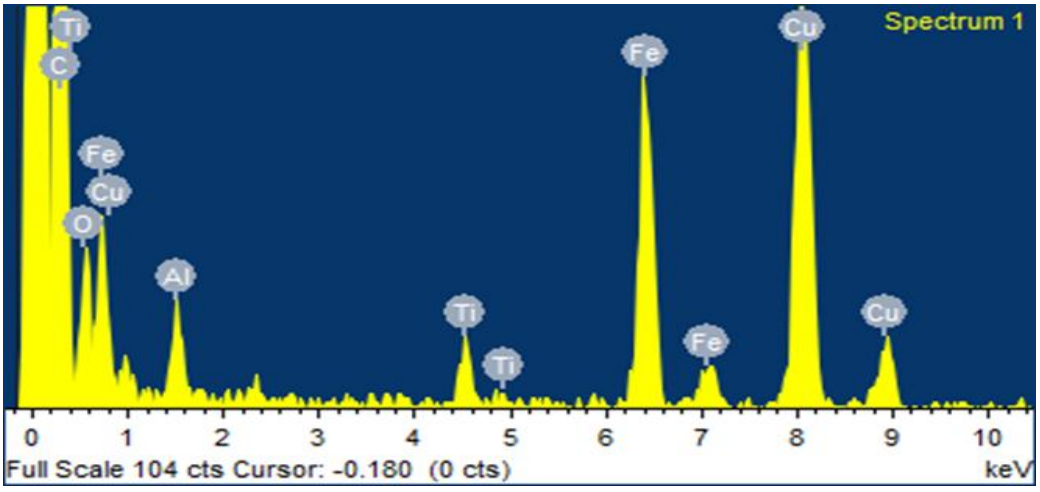




Element	Weight%	Atomic%	
C K	76.64	93.61	
Al K	0.89	0.48	
Fe K	22.47	5.90	
Totals	100.00		

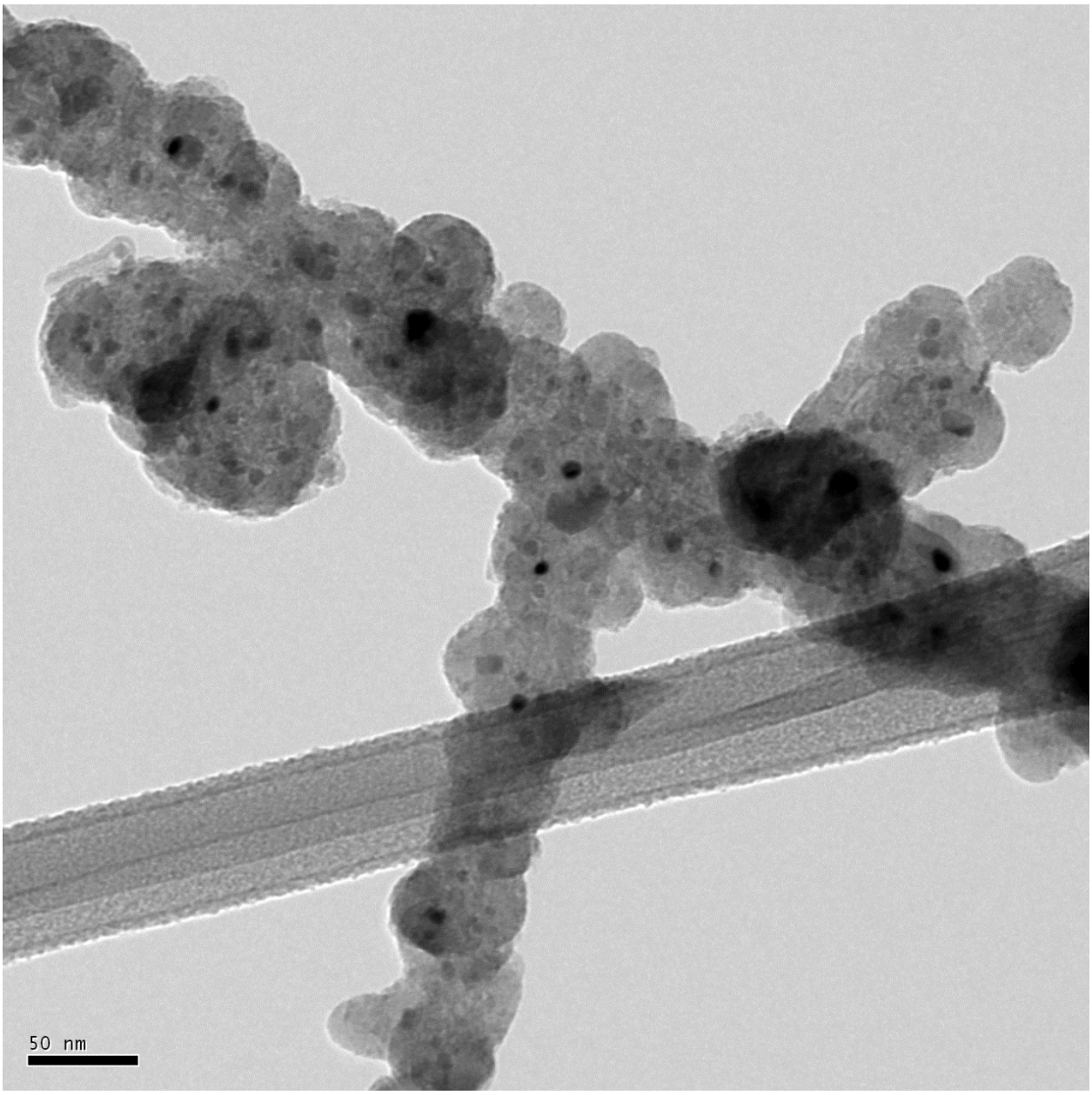
TEM and EDX of CNT-Ti



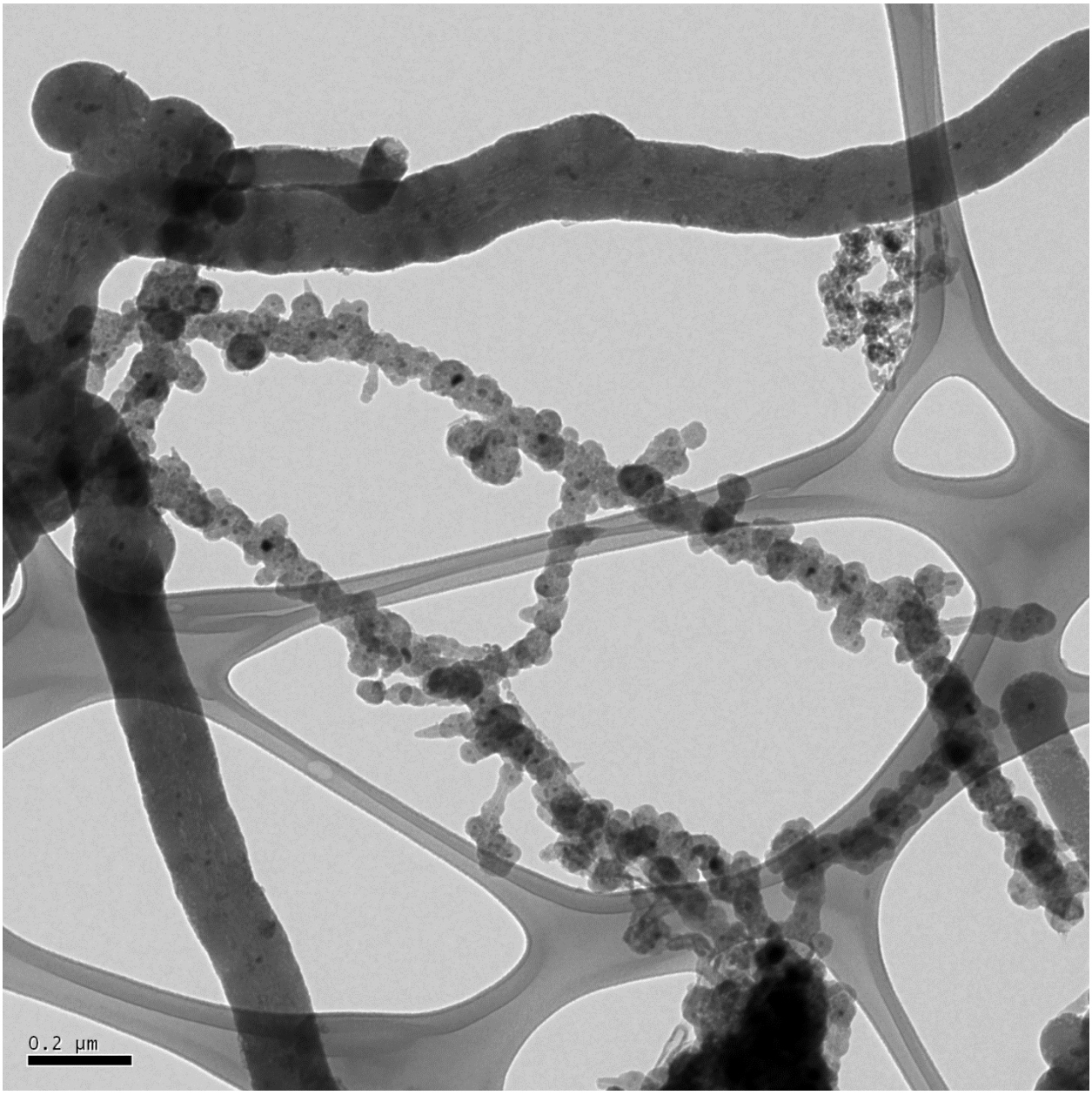


Element	Weight%	Atomic%	
C K	79.64	92.58	
O K	2.79	2.44	
Al K	1.90	0.98	
Ti K	2.08	0.61	

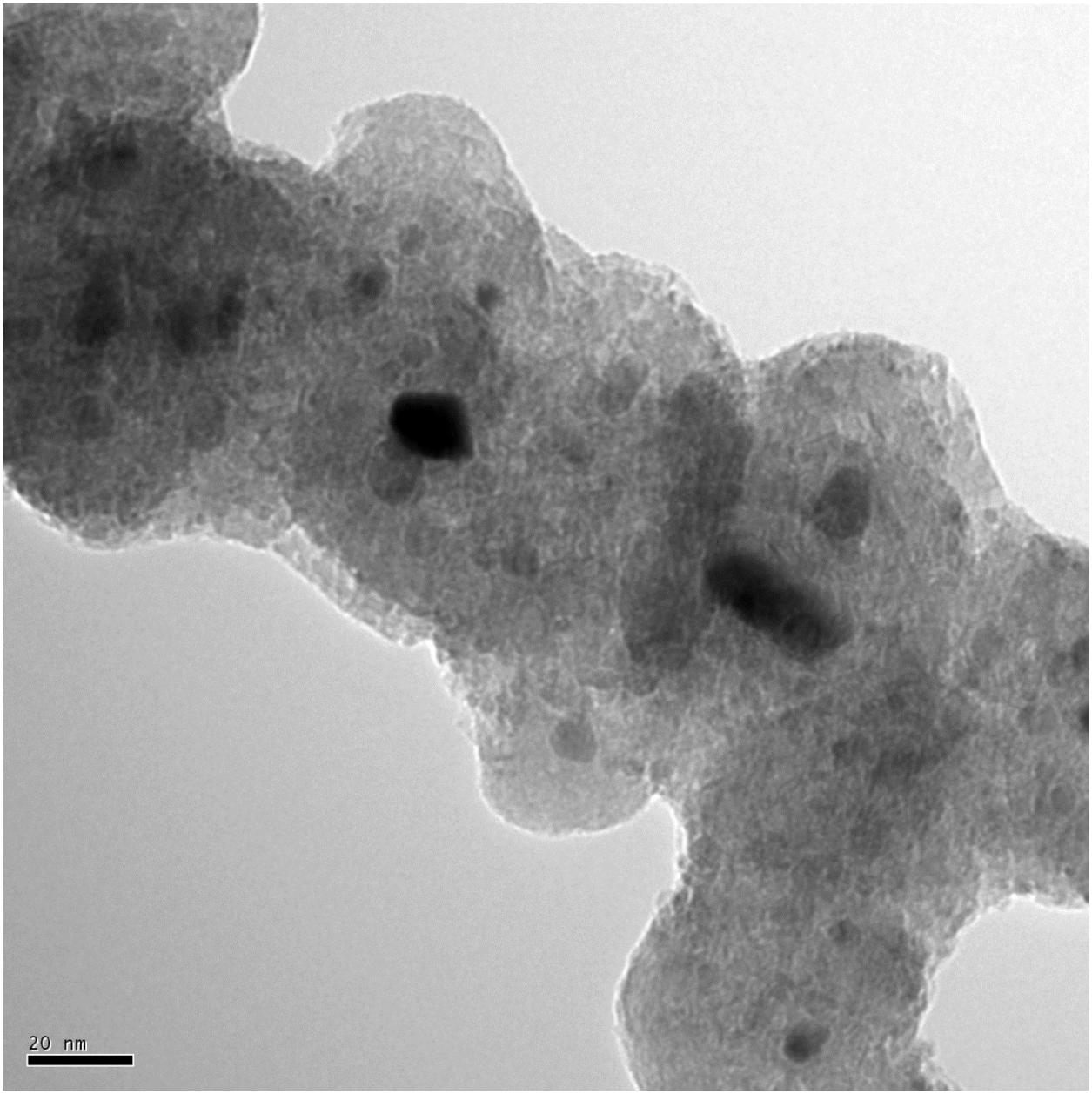
TEM of CNT-Ti



TEM of CNT-Ti



TEM of CNT-Ti



References

1. lithium/sulfur batteries, Journal of Power Sources 189, 1141–1146, 2009. Anna Glodek, Jozef M. Pacyn, Mercury Emission From Coal-Fired Power Plants In Poland , Atmospheric Environment 43, 5668–5673, 2009

2. http://www.corrosionsource.com/FreeContent/3/Combatting+Liquid+Metal+Attack+by+Mercury+in+Ethylene+and+Cryogenic+Gas+PlantsTask+1+-+Non-Destructive+Testing#Figure1 Combatting Liquid Metal Attack by Mercury in Ethylene and Cryogenic Gas PlantsTask 1 - Non-Destructive Testing

3. William W. Aljoe, Thomas J. Feeley ,Andrew P. Jones ,Candace Kairies Andrea T. McNemar ,Charles E. Miller, James T. Murphy, Mercury Capture and Fate Using Wet FGD at Coal-Fired Power Plants, U.S. Department of Energy, National Energy Technology Laboratory, Science Applications International Corporation, 2006

4. John Markovs, Des Plaines, Jack Corvini, Mercury Removal From Natural Gas & Liquid Streams; Gas Processors Association Annual Convention in San Antonio March 13-16, 2005

5. Guor-Cheng Fang, Yuh-Shen Wu, Tai-Hua Chang, Comparison Of Atmospheric Mercury (Hg) Among Korea, Japan, China An

6. W. F. Fitzgerald, C. H. Lamborg Geochemistry of Mercury in the Environment, Treatise on Geochemistry Volume 9, Pages 1–47

7. P. Li, X.B. Feng, G.L. Qiu, L.H. Shang, Z.G. Li, Mercury Pollution In Asia: A Review Of The Contaminated Sites, Journal of Hazardous Materials 168 (2009) 591–601

8. Elisabeth G. Pacyna, Jozef M. Pacyna, Frits Steenhuisen, Simon Wilson, Global anthropogenic mercury emission inventory for 2000, Atmospheric Environment 40 ,4048–4063, 2006.

9. E.G. Pacyna, J.M.Pacyna, K.Sundseth, J.Munthe , K.Kindbom, S.Wilson, F.Steenhuisen, P.Maxson, Global Emission Of Mercury To The Atmosphere From Anthropogenic Sources In 2005 And Projections To 2020, Atmospheric Environment 44, 2487–2499, 2010.

10. R. Duran, M. Ranchou-Peyruse, V. Menuet, M. Monperrus, G. Bareille, M.S. Gon, J.C. Salvado, D. Amouroux, R. Guyoneaud, O.F.X. Donard, P. Caumette , Mercury methylation by a microbial community from sediments of the Adour Estuary (Bay of Biscay, France), Environmental Pollution 156 951–958, 2008.

11. S. Mark Wilhelm Mercury in Petroleum and Natural Gas: Estimation of Emissions from Production, Processing, and Combustion, United States Environmental Protection Agency , EPA-600/R-01-066, September 2001.

12. P. Holmes, K.A.F. James, L.S. Levy, Is low-level environmental mercury exposure of concern to human health?, Science of the Total Environment 408 171–182, 2009.

13. Thomas W. Clarkson, Laszlo Magos The Toxicology of Mercury and its Chemical Compounds, Critical Review in Toxicology 36: 609-662, 2006
14. Anita Engqvist Mercury Exposure From Amalgam Fillings, ISBN 91–7045–458–2 ISSN 0346–7821, 1998.

15. Christianna Peterson, Mae Gustin, Seth Lyman, Atmospheric mercury concentrations and speciation measured from 2004 to 2007 in Reno, Nevada, USA, Atmospheric Environment 43 4646–4654, 2009.

16. www.atsdr.cdc.gov/toxprofiles/tp10-c8.pdf. Regulations and Guidelines Applicable to Mercury, Regulation and Advisories.

17. Guidance for Documenting Compliance with the 1ppb Limit on Mercury in Industrial Wastewater Discharges to Sewers, Commonwealth of Massachusetts Executive Office Of Energy & Environmental Affairs Department Of Environmental Protection, July, 2009

18. Report to Congress, U.S Environmental Protection Agency, Potential Export of mercury compounds from the United States for conversion to elemental Mercury, October 14, 2009.

19. www.fao.org/english/newsroom/news/2003/19783-en.html,UN Committee Recommends New Dietary Intake Limits For Mercury, Food and Agriculture Organization of the United Nation, 2003.

20. www.epa.gov/mercury/roadmap.htm, Addressing Mercury Uses in Products and Processes, EPA-HQ-OPPT-2005-0013, July 2006.
21. Public law 110-414- 110th Congress, An Act To Prohibit The Sale, Distribution, Transfer And Export Of Elemental Mercury And For Other Purposes, 122 STAT 4341 2008

22. Andrea Foster and Peter Carnel, Mercury Emissions control, Hydrocarbon Engineering , 2006.

23. Azman Shafawi, Les Ebdon, Mike Foulkes, Peter Stockwell and Warren Corns, Determination of total mercury in hydrocarbons and natural gas condensate by atomic fluorescence spectrometry, The Analyst, , 124, 185–189, 1999.

24. Daiane P. Torres , Ingrid M. Dittert , Heinrich Höhn , Vera L.A. Frescura , Adilson J. Curtius , Determination of mercury in gasoline diluted in ethanol by GF AAS after cold

vapor generation, pre-concentration in gold column and trapping on graphite tube , Microchemical Journal, Article on press, 2010.

25. Brice Bouyssiere, Yoana Nuevo Ordóñez, Charles-Philippe Lienemann, Dirk Schaumlöffel, Ryszard Lobninski, Determination of mercury in organic solvents and gas condensates by μflow-injection— inductively coupled plasma mass spectrometry using a modified total consumption micronebulizer fitted with single pass spray chamber, Spectrochimica Acta Part B 61 1063–1068, 2006.

26. S. Mark Wilhelm, LIAN Linag, Debrah Cussen and David A. Kirchessner, Mercury In Crude Oil Processed in the United States (2004), Environmental Science & Technology, 41, 4509-4514, 2007.

27. Masatoshi Morita, Jun Yoshinaga, John S . Edmondst, The Determination of Mercury Species in Environmental and Biological Samples, Pure & Appl. Chem., Vol. 70, No. 8, pp. 1585-1615, 1998.

28. Natural Gas Sector As A Significant Source of Global Mercury Supply and Emissions, Natural Resources Defense Council January 2011.

29. Hollebone, B.P. and C.X. Yang, Mercury in Crude Oil Refined in Canada, Environment Canada, Ottawa, ON, 2007.

30. Kerstin Leopold, Michael Foulkes, Paul Worsfold, Methods for the Determination and Speciation of Mercury in Natural Waters—A review, Analytica Chimica Acta 663, 127–138, 2010

31. Jianguo Chen, Hengwu Chen, Xianzhong Jin, Haiting Chen Determination Of Ultra-Trace Amount Methyl-, Phenyl- And Inorganic Mercury In Environmental And Biological Samples By Liquid Chromatography With Inductively Coupled Plasma Mass Spectrometry After Cloud Point Extraction Preconcentration, Talanta 77 1381–1387, 2009.

32. Jorgelina C.A. Wuilloud, Rodolfo G. Wuilloud, Anne P. Vonderheide, Joseph A. Caruso, Gas Chromatography/Plasma Spectrometry—An Important Analytical Tool For Elemental Speciation Studies, Spectrochimica Acta Part B 59 755– 792, 2004.

33. Hakan an Emteborg, James Snell, Jin Qian, and Wolfgang Frech, Sources Of Systematic Errors in Mercury Speciation Using Grignard Reagents and Capillary Gas Chromatography Coupled To Atomic Spectrometry Chemosphe Vol. 39 No. 7, 1137-1152, 1999.

34. Mariana A. Vieira, Patricia Grinberg, Cláudio R.R. Bobeda, Mariela N.M. Reyes, Reinaldo C. Campos, Non-Chromatographic Atomic Spectrometric Methods in Speciation Analysis: A Review Spectrochimica Acta Part B 64 459–476, 2009.

35. Lian Liang, Nicolas S. Bloom, and Milena Horvat, Simultaneous Determination of Mercury Speciation in Biological Materials by GC/CVAFS After Ethylation and Room-Temperature Precollection, Clinical Chemistry,Vol. 40, No. 4, 602-607, 1994.

36. Yingjie Li, Bin Hu, Sequential Cloud Point Extraction For The Speciation Of Mercury In Seafood By Inductively Coupled Plasma Optical Emission Spectrometry Spectrochimica Acta Part B 62 1153–1160, 2007.

37. James Snell, Jin Qian, Magnus Johansson, Kees Smit and Wolfgang Frech, Stability and Reactions of Mercury Species in Organic Solution, Analyst, Vol. 123, 905–909, 1998.

38. Brice Bouyssiere, Franck Baco,Laurent Savary, Ryszard Lobinski, Speciation Analysis For Mercury In Gas Condensates By Capillary Gas Chromatography With Inductively Coupled Plasma Mass Spectrometric Detection, Journal of Chromatography A, 976, 431–439, 2002.

39. Chris F. Harrington The Speciation Of Mercury And Organomercury Compounds By Using High-Performance Liquid Chromatography, Trends in Analytical Chemistry, vol. 19, nos. 2+3, 167-179, 2000.

40. Biyang Deng, Yan Xiao, Xiangshu Xu, Pingchuan Zhu, Shaojun Liang,Weiming Mo, Cold Vapor Generation Interface For Mercury Speciation Coupling Capillary Electrophoresis With Electrothermal Quartz Tube Furnace Atomic Absorption Spectrometry: Determination Of Mercury And Methylmercury, Talanta 79 1265–1269, 2009.

41. Malcolm P. Heyward*a, Robert L. Hurlea and Bjoern Sauerhammerb Determination of the Recovery of Dimethylmercury and Diphenylmercury Extracted From Organic Solvents and a Liquid Condensate With Bromine Water Using Cold Vapor Atomic Absorption Spectrometry, Analytical Communications, Vol 34, 279–281, 1997.

42. Stephane Guedron, Sylvain Grangeon, Bruno Lanson, Michel Grimaldi, Mercury Speciation in A Tropical Soil Association; Consequence of Gold Mining on Hg Distribution in French Guiana, Geoderma 153 331–346, 2009.

43. N. S. Bloom, Analysis And Stability Of Mercury Speciation In Petroleum Hydrocarbons, Fresenius J Anal Chem 366 :438–443, 2000.

44. Haiting Chen, Jianguo Chen, Xianzhong Jin , Danyi Wei, Determination Of Trace Mercury Species By High Performance Liquid Chromatography–Inductively Coupled Plasma Mass Spectrometry After Cloud Point Extraction, Journal of Hazardous Materials 172, 1282–1287, 2009.

45. Yunjun Wang ,Yufeng Duan, Liguo Yang, Changsui Zhao, Xianglin Shen, Mingyao Zhang, Yuqun Zhuo, Changhe Chen, Experimental Study On Mercury Transformation

And Removal In Coal-Fired Boiler Flue Gases, Fuel Processing Technology 90 , 643–65, 2009.

46. UOP Method 938-10, Total Mercury and Mercury Species in Liquid Hydrocarbons.

47. Michael L. Braden, Mercury: Real Problems Not Roman Mythology, Nalco Company, Energy Services Division

48. Himanshu Agarwal, Divyanshi Sharma, Susheel Kumar Sindhu, Sonika Tyagi,Saiqa Ikram, Removal Of Mercury From Wastewater Use Of Green Adsorbents - A Review, Electronic Journal of Environmental, Agricultural and Food Chemistry , 9, 1551-1558, 2010.

49. Aaron Hutchison, David Atwood, Q. Eduardo Santilliann-Jimine, The Removal of Mercury from Water by Open Chain Ligands Containing Multiple Sulfurs, Journal of Hazardous Materials 156, 458–465, 2008.

50. M. Zabihi, A. Ahmadpour, A. Haghighi Asl, Removal of Mercury from Water by Carbonaceous Sorbents Derived From Walnut Shell, Journal of Hazardous Materials 167, 230–236, 2009.

51. Rıdvan Say, Ebru Birlik, Zerrin rdemgil, Adil Denizli, Arzu Ersoz, Removal Of Mercury Species With Dithiocarbamate-Anchored Polymer/Organosmectite Composites, Journal of Hazardous Materials 150, 560–564, 2008.

52. H. Bessbousse, T. Rhlalou, J.-F. Verchere, L. Lebrun, Mercury Removal from Wastewater Using A Poly(Vinylalcohol)/Poly(Vinylimidazole) Complexing Membrane, Chemical Engineering Journal 164, 37–48, 2010.

53. KUANG Min, YANG Guo-hua, CHEN Wu-jun, ZHANG Zhi-xue, Study On Mercury Desorption From Silver-Loaded Activated Carbon Fiber And Activated Carbon Fiber, Journal Of Fuel Chemistry And Technology, Volume 36, Issue 4, 468-473, 2008.

54. Jianzhong Zhu, Baolin Deng, John Yang, Dianchen Gang, Modifying Activated Carbon With Hybrid Ligands for Enhancing Aqueous Mercury Removal, Carbon 47, 2014-2-25, 2009.

55. Philippe Serp, Massimiliano Corrias, Philippe Kalck, Carbon Nanotubes and Nanofibers in Catalysis, Applied Catalysis A: General 253, 337–358, 2003.

56. Samia A. Kosa, Ghalia Al-Zhrania, Mohamed Abdel Salam, Removal Of Heavy Metals From Aqueous Solutions By Multi-Walled Carbon Nanotubes Modified With 8-Hydroxyquinoline, Chemical Engineering Journal , 2011.

57. Amjad H. El-Sheikh, Yahya S. Al-Degs, Randa M. Al-As'ad, Jamal A. Sweileh Effect Of Oxidation And Geometrical Dimensions Of Carbon Nanotubes On Hg(II) Sorption And Preconcentration From Real Waters, Desalination 270, 214–220, 2011.

58. www.naturalgas.org/naturalgas/processing_ng.asp. Processing Natural Gas

59. John Markovs , Des Plaines, Illinois, Jack Corvini, Mercury Removal From Natural Gas & Liquid Streams, UOP.

60. E. Clegg, Measurements of The Interface Between 5083 Aluminum And Liquid Mercury Using Impedance Spectroscopy, Corrosion Science 52 4028–4034, 2010.

61. Azman Shafawi, Les Ebdon, Mike Foulkes, Peter Stockwell,Warren Corns, Preliminary Evaluation of Adsorbent-Based Mercury Removal Systems For Gas Condensate, Analytica Chimica Acta 415, 21–32, 2000.

62. Giacomo Corvini, Julie Stiltner and Keith Clark, Mercury Removal From Natural Gas And Liquid Streams, UOP LLC Houston, Texas, USA

63. Omar M. Baageel , Gas Plant Solves Hg Problems With Copper-Sulfate Absorbent, Oil and Gas Journal, 2010. http://www.ogj.com/articles/print/volume-108/issue-19/technology/gas-plant-solves-hg.html

64. www.selectiveadsorption.com, Mercury Removal Adsorbent for Use With Liquid Hydrocarbons, Air, Hydrogen and Other Gases.

65. www.axens.net Trapping Material For Mercury Removal From Gases And Liquid .

66. www.calgoncarbon.com, Impregnated Activated Carbon to Remove Aliphatic and Liquid Hydrocarbon.

67. www.nucon-int.com, MERSORB® Mercury Adsorbents, Nucaon Mersorb ® Bulletin 11B28, 2010

68. ZHANG An-chao, SUN Lu-shi, XIANG Jun, HU Song, FU Peng, Su Sheng, ZHOU Ying-biao, Removal of Elemental Mercury From Coal Combustion Flue Gas By Bentonite-Chitosan and Their Modifier, Journal Of Fuel Chemistry And Technology,37,4, 489-495, 2009.

69. Junwei Wang, Jianli Yang, Zhenyu Liu, Gas-Phase Elemental Mercury Capture By A V2O5/AC Catalyst, Fuel Processing Technology 91, 676–680, 2010.

70. Qi Wan, Lei Duan, Kebin He, Junhua Li, Removal of Gaseous Elemental Mercury Over a CeO2–WO3/TiO2 Nanocomposite In Simulated Coal-Fired Flue Gas, Chemical Engineering Journal 170, 512–517, 2011.

71. Haiqiang Wang, Siyao Zhoua, Ling Xiao, Yuejun Wang, Yue Liua, Zhongbiao Wua, Titania Nanotubes—A Unique Photocatalyst And Adsorbent For Elemental Mercury Removal, Catalysis Today 175, 202– 208, 2011.

72. Gary Gildert, Hasan Ali Karavacıoglu, Peter J H Carnell, Mercury Removal from Liquid Hydrocarbons in Ethylene Plants , AIChe Number 135C 2010 Spring, National Meeting, San Antonio, TX, 2010 http://apps.aiche.org/proceedings/Abstract.aspx?PaperID=175926March

73. Peter J H Carnell, Steve Willis, Mercury Removal From Liquid Hydrocarbons, http://www.eptq.com/view_article.aspx?intAID=190, 2005.

74. Peter J, Carnell, Vince A Row, A Re-Think of The Mercury Removal Problem for LNG Plants, Johnson Matthey Catalysts, www.jmcatalysts.com, 2007.

75. S. Mark Wilhelm, Nicolas Bloom, Review, Mercury in Petroleum, Fuel Processing Technology 63, 1–27, 2000.

76. Neil Eckersley, Des Plaines, Mercury Removal From Gaseous and Liquid Hydrocarbons, UOP LCC , 2011

77. Muhamad, Rashid Sainal, Azman, Shafawi, Abdul Jabar Mohamed, Mercury Removal System for Upstream Application: Experience in Treating mercury From Raw Condensate, Society of Petroleum Engineer, SPE 106610, 2007.

78. Muhamad, Rashid Sainal, T.Mohd Uzaini, Azman, Shafawi, Abdul Jabar Mohamed, Mercury Removal Project: Issues and Challenges in Managing and Executing A Technology Project, Society of Petroleum Engineer, SPE 110118 2007.

79. Martin Rose, Michael Knaggs, Linda Owen and Malcolm Baxter, A Review Of Analytical Methods For Lead, Cadmium, Mercury, Arsenic And Tin Determination Used In Proficiency Testing, J. Anal. At. Spectrom., 16, 1101–1106, 2001.

80. World Health Organization Regional Office for Europe Air Quality Guidelines, Second Edition, Chapter 6.9, 157-161, 2000.

81. Joanna Szpunar, Ryszard Tobinski, Hyphenated Techniques in Speciation Analysis, Metal Speciation in Petroleum-Related Samples, Chapter 12, 135-141, 2007.

82. http://www.nap.edu/openbook.php?record_id=9899&page=32, Toxicological Effects of Methylmercury, The National Academies , 2000.

83. Samorn Hirunpraditkoon, Nathaporn Tunthong, Anotai Ruangchai, and Kamchai Nuithitikul, Adsorption Capacities of Activated Carbons Prepared from Bamboo by KOH Activation, World Academy of Science, Engineering and Technology 78, 711-715, 2011.

84. Azman Shafawi, Les Ebdon, Mike Foulkes, Peter Stockwell, Warren Corns, Preliminary Evaluation of Adsorbent-Based Mercury Removal Systems for Gas Condensate, Analytica Chimica Acta 415, 21–32, 2000.

85. William J. O'Dowd , Richard A. Hargis, Evan J. Granite, Henry W. Pennline, Recent Advances in Mercury Removal Technology at the National Energy Technology Laboratory, Fuel Processing Technology 85 533– 548, 2004.

86. Nick Soelberg, Joe Enneking, Carbon Bed Mercury Emissions Control for Mixed Waste Treatment, Journal of the Air & Waste Management Association, Volume 60, 60:1341–1352, 2010.

87. Peter J.H Cornell, Andrea, Foster, Jon Gregory Mercury Matters. Mercury Matters, Johnson Matthey Catalysts, UK, 2005.

88. Xuemei Ren, Changlun Chen, Masaaki Nagatsu, Xiangke Wang, Carbon Nanotubes As Adsorbents In Environmental Pollution Management: A Review , Chemical Engineering Journal 170, 395–410, 2011

89. M. Ahmaruzzaman, A Review on The Utilization of Fly Ash, Progress in Energy and Combustion Science 36, 327–363, (2010)

90. Ignacio Martin-Gullon, Jose Vera, Juan A. Conesa, Jose L. Gonzalez, Cesar

91. Catalysts In A Floating Catalyst Reactor, Carbon 44, 1572–1580, 2006.

92. Joao Valente Nabais, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Marisa Belchior, Dulce Boavida, Tatiana Diall , Ibrahim Gulyurtlu, Mercury Removal From Aqueous Solution and Flue Gas By Adsorption On Activated Carbon Fibres, Applied Surface Science 252, 6046–6052, 2006

93. Zhijian Mei, Zhemin Shen, Qingjie Zhao, Wenhua Wang, Yejian Zhang, Removal And Recovery Of Gas-Phase Element Mercury By Metal Oxide-Loaded Activated Carbon, Journal of Hazardous Materials 152 721–729, 2008

94. Xuemei Ren, Changlun Chen, Masaaki Nagatsu, Xiangke Wanga, Carbon Nanotubes As Adsorbents In Environmental Pollution Management: A review, Chemical Engineering Journal 170 395–410, 2011

95. K. Anoop Krishnan, T.S. Anirudhan Removal Of Mercury(II) From Aqueous Solutions And Chlor-Alkali Industry Effluent By Steam Activated And Sulphurised Activated Carbons Prepared From Bagasse Pith: Kinetics And Equilibrium Studies, Journal of Hazardous Materials B92 161–183, 2002

96. G. Skodras, Ir. Diamantopoulou, G.P. Sakellaropoulos, Role Of Activated Carbon Structural Properties And Surface Chemistry In Mercury Adsorption, Desalination 21,281–286, 2007

97. Xiao Liang,Zhaoyin Wen, Yu Liu, Hao Zhang, Jun Jin, Meifen Wu, Xiangwei Wu A Composite of Sulfur And Polypyrrole–Multi Walled Carbon Combinatorial Nanotube as Cathode for Li/S Battery, Article in Press, Journal of Power Sources, 2012.

98. Juchen Guo, Yunhua Xu, and Chunsheng Wang Sulfur-Impregnated Disordered Carbon Nanotubes Cathode for Lithium Sulfur Batteries, Nano Letters 11, 4288–4294, 2011

99. Lixia Yuan, Huiping Yuan, Xinping Qiu∗, Liquan Chen,Wentao Zhu, Improvement of cycle property of sulfur-coated multi-walled carbon nanotubes composite cathode for

VITA

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I was born in Bani Malik area, that near Taif. I grew up there until I finished the high school in 1982. Then, I moved to Jeddah to peruse my BS degree in chemistry at King Abdulaziz University. I Joined Saudi Aramco in 1988.

Education

BS in chemistry, King Abdulaziz University, 1987
Two years special program at Colorado School of Mines, Colorado, USA 1990-1992
MS degree in chemistry from KFUPM, October 2004
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Work Experience.

I Joined Saudi Aramco in 1988 and since then I have been working with Research and Development Center. I have gone through various technical and management development at different units at the center covering activities of upstream and downstream crude oil operations. Currently, I am research science consultant at Reserch and Development Center

Conferences.

I have been an active member of the American chemical society. I was chair of the local chapter of American chemical society in addition being a board member for several years. I have participated in organizing committee of about four conferences of International Conference and Exhibition on Chemistry in Industry. I was the chairman of the 2007 International Conference of Chemistry in Industry, Chemindix-2007

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